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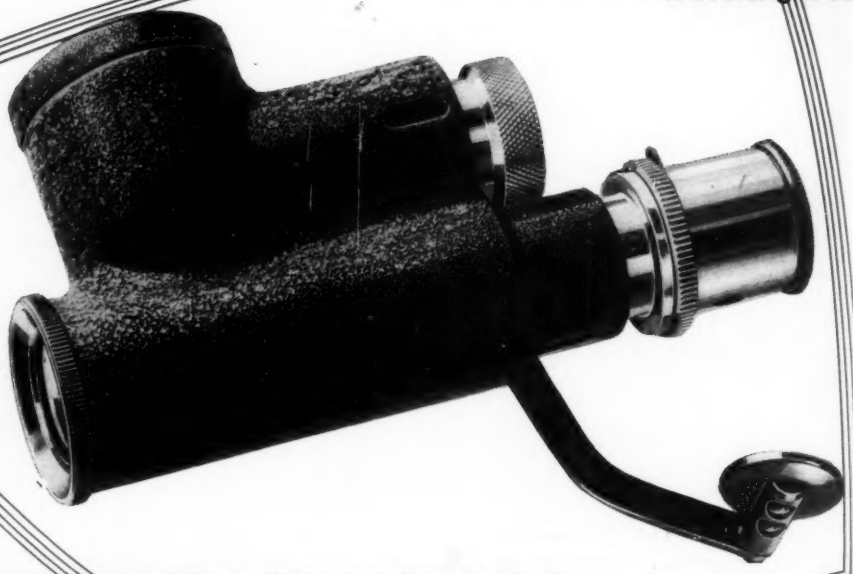

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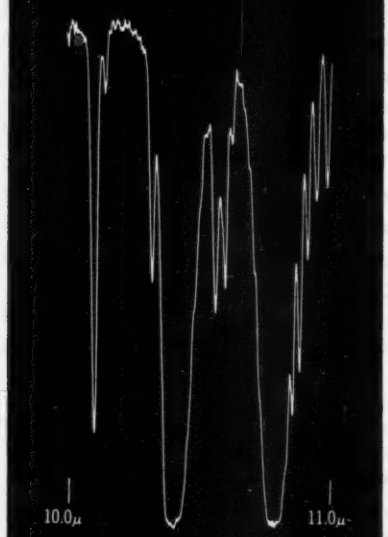

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Editor's Outlook

THE opinion is commonly held that high-school enrollments in science have been falling off during the last several decades, to the advantage of certain other subjects, particularly social studies. To ascertain the facts and the possible underlying reasons the Central Association of Science and Mathematics Teachers appointed a Committee on the Significance of Mathematics and Science in Education. Its final report, in the February number of *School Science and Mathematics*, should be read by all who are concerned with the implications of this important question.

It shows that from 1922 to 1952 enrollments in physics dropped from 8.93 per cent of all high-school students to 4.30; in chemistry they increased only from 7.40 to 7.60, but in biology from 8.78 to 20.40. At the same time, enrollments in "other sciences," which really means general physical science, had increased in 1952 to 3.80 per cent. The situation in mathematics is not quite so clear; enrollments in "generalized" courses have increased, while, on the whole, they have dropped in the specialized courses.

Relative enrollments have therefore remained substantially the same, in biology they have increased considerably, while the drop in physics is practically offset by increases in generalized physical science. Nevertheless, this average, over-all picture is not considered altogether satisfactory by the Committee, in view of the recognized increases in the importance of science and since their statistical studies show that science courses taken in high school do not in general increase the *interest* of students in these fields.

In the belief that the failure may be due to inadequately trained teachers, the Committee investigated the background and training of high-school teachers of science and mathematics and the requirements for their certification. To quote from the report:

> The findings of these studies indicated that (1) teachers are invariably trained significantly better in one field of science than in the others; (2) although beginning teachers usually teach generalized courses in science, and in small schools may teach all the science, their training in science is not suited to such teaching; (3) that the subject-matter competencies of new science teachers tend to be factual rather than centered around the ability to apply and make use of scientific information; (4) there is little uniformity in state requirements for certifying teachers of science, since at least seven states have not established requirements while others demand as much as forty semester hours to teach in certain areas of science; (5) there seems to be little evidence that certifying agencies have considered the qualifications desirable for supervisors or consultants in the areas of science; and (6) a comparison of state requirements with the recommendations of various authoritative bodies indicates that in general there are great discrepancies between what is considered desirable and the actual training in science that teachers receive.

The Committee supports the now common organization of the curriculum in which generalized science instruction is given on a required basis to all pupils up through the tenth grade. Beyond this, specialized courses such as chemistry and physics are offered on an elective basis. However, these specialized courses are all too commonly considered as parts of an entirely different educational sequence, with different objectives from those of generalized science. The drop in interest and enrollment at this stage could be prevented, it is believed, if a closer relation were established.

> If the more successful educators in mathematics and science firmly back the idea of generalized mathematics and science and help to build and teach such courses, probably many students who now find the higher courses difficult, will find them less difficult and will decide to elect them.

It is pointed out, with good reason, that too few teachers are broadly enough trained in science to teach the generalized courses. These classes are often assigned indiscriminately, with little regard to the teacher's interest in the subject and possible effectiveness. Under such circumstances pupils are not likely to be inspired to continue further.

A final paragraph from the report will point up the issue:

> The committee at this point would like to emphasize that the recommendations made so far will demand cooperative and concerted action on the part of all professional persons concerned with mathematics and science education. Such persons include scientists, educators, mathematicians, and others specializing in the methodologies of mathematics and science education. Unfortunately, such cooperation is not always evident.

The implication of the last sentence should sink into the mind of the chemical profession, which has so often expressed itself as greatly concerned with this problem.

CHEMISTRY IN THE STRATOSPHERE AND UPPER ATMOSPHERE[1]

LEWIS E. MILLER
Geophysics Research Directorate, Air Force Cambridge Research Center, Air Research and Development Command, Cambridge, Massachusetts

OUR knowledge concerning the earth's upper atmosphere has increased rapidly during comparatively recent years. The Geophysics Research Directorate, U. S. Air Force Cambridge Research Center, the U. S. Naval Research Laboratory, and the U. S. Signal Corps conduct upper atmospheric studies in their own laboratories and support other investigations at various universities throughout the country. The study of the upper atmosphere is of great scientific and practical importance. The stratosphere may well become the world's air highways of tomorrow. With increasing studies this region as well as the higher regions are fast becoming familiar layers in the earth's upper atmosphere.

The influence of the physical and chemical characteristics of the upper atmosphere upon the human body is of paramount significance in the design of safe and adequately protected aircraft. Aero-medical investigations, to cite but one illustration, are concerned about the potential hazards of high-altitude flight due to the presence of primary cosmic ray particles found at an altitude of about 18 to 20 kilometers. Studies of the ozone layer have led to an understanding of its beneficial effect in shielding and protecting us from the serious solar ultraviolet radiations.

[1] Presented at the 124th Meeting of the American Chemical Society, Chicago, September, 1953.

NOMENCLATURE

Various names have been proposed to characterize the different regions and levels of the atmosphere (*1*, *2*, *3*). Classification of atmospheric levels may be made on the basis of composition. The *homosphere* is defined as that region from the surface of the earth up to a level of about 100 kilometers where composition first begins to change materially. The *heterosphere* is

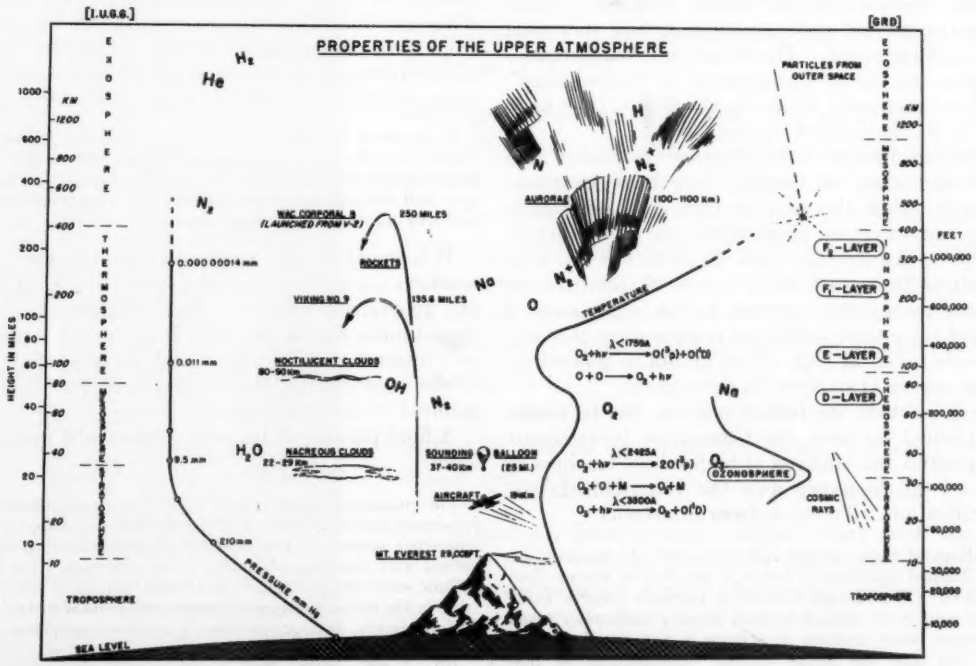


Figure 1. Properties of the Upper Atmosphere

The values on the pressure curve, 210 mm., 9.5 mm., 0.011 mm., and 0.00000014 mm., are given for the heights 10 km., 30 km., 80 km., and 220 km., respectively.

used to denote the region of different composition due to processes of diffusion and molecular dissociation. Commonly in geophysics the characterization of the terrestrial atmosphere is described on the basis of temperature classification. Accordingly, the atmosphere is divided into a series of non-concentric shells, *troposphere* (0 to 11 km.), the *stratosphere* (11 to 35 km.), the *mesosphere* (35 to 80 km.), the *thermosphere* (80 to 400 km.), and the *exosphere* (above 400 km.) (see Table 1). It should be emphasized that there is no well defined line of demarcation separating the various layers. The layer heights vary seasonally and latitudinally as well as with atmospheric conditions. The above heights are given for latitude 45° north or south. The suffix, "pause," is employed to signify an upper boundary. Thus the *tropopause* is the boundary region between the troposphere and the stratosphere. The height of the tropopause varies widely with latitude, being about 7 to 8 km. at the poles and about 18 km. at the equator.[2]

The troposphere is the lowest atmospheric layer. In this region the average temperature gradient is negative, decreasing from the temperature at the surface of the earth to a minimum at an altitude of about 20 km. The stratosphere was originally named by the French scientist Leon Philippe Teisserne de Bort in 1909 who defined it as the nearly isothermal layer above the troposphere. The mesosphere is the layer between the stratosphere and the deep temperature minimum at about 80 km. It is sometimes convenient to use other names to characterize certain regions of the atmosphere. The *ozone layer*, or *ozonosphere*, has often been applied to the level where the ozone concentration is greatest. The *chemosphere* (30 to 80 km.) is convenient to use for the region where photochemical reactions become important in the upper atmosphere.

The stratosphere and upper atmosphere are practically free of any cloud formations, except on rare occasions when "mother-of-pearl" (or nacreous) clouds (22 to 28 km.) and noctilucent clouds (80 to 90 km.) appear. The *ionosphere*, as the name implies, is the region characterized by the formation of ions by the action of solar radiations upon the atmospheric constituents. It is composed of at least four distinct layers known as the *D*-region and the *E*-, F_1-, and F_2-layers, while some workers have postulated a *G*-layer. These layers in the ionosphere are of practical importance in radio communication since they reflect, refract, and absorb radio waves.

The exosphere refers to the high outermost region of the atmosphere. Within this region the gaseous particles are moving with great velocity and the mean free path is very large before colliding with other particles. Some of the lighter constituents, such as helium, actually escape from the earth's atmosphere.

[2] This classification is based upon the recommendation of the committee on nomenclature of the International Union of Geodesy and Geophysics (I. U. G. G.). The Geophysics Research Directorate (GRD) Air Force Cambridge Research Center uses a slightly different terminology. For the comparison see Figure 1.

TABLE 1
Layers of the Terrestrial Atmosphere

Layer	*Height range, km.*	*Boundary region*
Troposphere	0–11	Tropopause
Stratosphere	11–35	Stratopause
Mesosphere	35–80	Mesopause
Thermosphere	80–400	Thermopause or "critical level"
Exosphere	400 outward	

NOTE: The heights are given as average values for latitude 45° north or south.

Within the mesosphere and ionosphere the awe-inspiring phenomenon and luminescence of the aurorae occur. Auroral spectra furnish us with most valuable information concerning the component gases present and their state of occurrence in the high regions of the atmosphere. Various divisions of the atmosphere are summarized in Figure 1. The term *upper atmosphere* is used very widely by some investigators. It has various meanings depending upon the context. For example, the weather forecaster may use this term to describe the upper troposphere, while the radio engineer and others may employ it to mean the regions above the stratosphere. The latter meaning will be used in this paper.

GRAVITATIONAL DIFFUSION

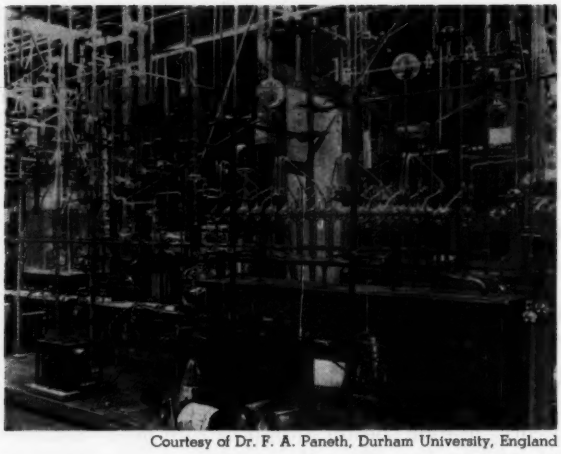
One of the main problems in the study of the upper atmosphere is the vertical distribution of the constituent gases and their pressures. In order to carry out calculations it is necessary to know approximately the height at which diffusive equilibrium of the constituent gases under the action of gravity begins to be important.

An ideal atmosphere in the absence of mixing will obey Dalton's law of partial pressures. The vertical distribution and diffusion of each constituent is independent of the presence of the other constituents. Such an atmosphere would eventually stratify, the lighter gases escaping the gravitational attraction of the earth while the heavier ones would be found in the lower layers of the atmosphere. As early as 1804 when Gay-Lussac (*4*) analyzed samples of air obtained in a balloon flight at an altitude of about 6.5 km. scientists have been interested in testing this law experimentally.

Assuming the earth's atmosphere to be at rest with no disturbing external factors the vertical distribution of a gas is expressed by the following well known exponential equation of Dalton:

$$\frac{d \log (\rho T)}{dz} = -\frac{mg}{kT}$$

where T is the temperature in degrees Kelvin, k is Boltzmann's constant, m the molecular mass in grams, g the acceleration due to gravity, z the altitude, and ρ is the density of the constituent considered. The quantity kT/mg which has the dimensions of length is usually expressed as the *scale height* (the height of a



Courtesy of Dr. F. A. Paneth, Durham University, England

Figure 2. Apparatus for the Microanalysis of Rare Gases as Employed at Durham University, England

The charcoal absorption fractionation column for the separation of helium and neon is shown in the foreground.

homogeneous atmosphere) and is denoted by the symbol H. The above equation becomes

$$\frac{d \log (\rho T)}{dz} = -\frac{1}{H}$$

This equation provides the useful relationship between the density distribution and the temperature distribution, from which if one is known experimentally the other may be deduced. Assuming an isothermal atmosphere the integrated equation can be expressed as follows:

$$\frac{\rho}{\rho_0} = e^{-z/H}$$

TABLE 2
Methods of Probing the Upper Atmosphere

Method	*Height range, km.*	*Information obtainable*
	Direct measurements	
Sounding balloon	0–40	Composition, wind, pressure, temperature
Aircraft	0–18	Same as balloon
Rocket-sondes	0–400	Density, pressure, temperature, composition, solar spectra
Mother-of-pearl clouds	22–29	Wind velocities, H_2O vapor
Noctilucent clouds	80–90	Wind velocities
	Indirect methods	
Abnormal sound propagation	35–60	Density, pressure, temperature, wind
Searchlight techniques	10–65	Density (hence temperature)
Meteor trails	40–150	Density, pressure, temperature, wind
Spectral studies:		
Ultraviolet	20–70	Ozone, composition, temperature
Infrared	?	Composition, temperature
Night sky	60–700	Composition, temperature
Aurorae	80–1100	Composition, temperature
Theoretical studies	800 outward	Fringe of atmosphere

Actually the conditions in the upper atmosphere are far from ideal owing to turbulence, atmospheric tides, temperature inversions, and wind systems. Lettau (*5*) has calculated that the time required for the transformation of complete mixing into a Dalton atmosphere is a matter of years below 100 km. altitude. According to theory it is not until a much higher altitude is reached that gravitational diffusion becomes appreciably effective.

At the present time the latest experimental data upon gravitational separation of atmospheric components have been obtained by F. A. Paneth (*6*, *7*, *8*) in collaboration with scientists in the Department of Aeronautical Engineering, University of Michigan. Samples of air are obtained in steel cylinders of about 8 liters capacity. These are equipped with automatic sampling devices and carried into the upper atmosphere by Aerobee rockets to heights of about 70 km. The rocket flights are made at White Sands, New Mexico. After being retrieved these upper air samples are sent to and analyzed by Paneth and co-workers at the University of Durham, England (see Figure 2). No more than about one cubic centimeter of air at NTP is contained in the 8-liter sampling flask.

The method employed by Paneth in analysis is a micro procedure of repeated fractional absorption of the rare gases, helium, neon, and argon on charcoal. The experimental results obtained are apparently contradictory to those predicted from theory. Up to 60 km. no change in the percentage composition of the atmosphere was found. Above this limit, for the first time and from independent samples collected on rocket flights over White Sands during December 1950 and September 1951, Paneth found that the ratios of helium, neon, and argon to nitrogen changed consistently to indicate a definite gravitational separation. In a private communication from Dr. Paneth from analyses yet unpublished on rocket samples collected during 1952 by the Michigan team, the results show significant variations of composition in good agreement with those already published.

PHYSICAL PROPERTIES

New and improved methods of probing the upper atmosphere, especially since the war, have yielded much valuable information. New discoveries of a previously unsuspected nature have stimulated an increasing interest in the physical and chemical composition of the upper atmosphere to hitherto unknown heights. In Table 2 is shown a brief summary of present day methods for the exploration of the upper atmosphere. Each method has its advantages and disadvantages.

Pressures in the High Atmosphere. Pressure at 100 km. altitude is about 10^{-3} mm. of Hg which is about the same as in an ordinary electric light bulb. At 300 km. the pressure is of the order of 10^{-6} mm., the pressure attained by the best modern vacuum pumps. The aerodynamicist is particularly interested in pressures and the mean free path between collisions. These

TABLE 3
Atmospheric Data Compiled from Current Sources[a]

Height, km.	*Temperature (μ = 28.966), °K.*	*Pressure, mm. Hg*	*Density, g./cm.³*	*Number density, cm.⁻³*	*Mean free path, cm.*
0	288.0	7.6×10^{2}	1.1×10^{-3}	2.6×10^{19}	8.6×10^{-6}
10	230.8	2.1×10^{2}	4.2×10^{-4}	8.8×10^{18}	2.1×10^{-5}
20	212.8	4.2×10^{1}	9.3×10^{-5}	2.0×10^{18}	9.7×10^{-5}
30	231.7	9.5×10^{0}	1.9×10^{-5}	3.9×10^{17}	4.8×10^{-4}
40	262.5	2.4×10^{0}	4.2×10^{-6}	6.8×10^{16}	2.2×10^{-3}
50	270.8	7.6×10^{-1}	1.2×10^{-6}	2.3×10^{16}	7.8×10^{-3}
60	252.8	2.2×10^{-1}	3.5×10^{-7}	$8.[illegible] \times 10^{15}$	2.6×10^{-2}
70	218.0	5.5×10^{-2}	9.7×10^{-8}	2.5×10^{15}	9.3×10^{-2}
80	205.0	1.1×10^{-2}	2.1×10^{-8}	3.9×10^{14}	4.3×10^{-1}
90	217.0	2×10^{-3}	4.1×10^{-9}	8.7×10^{13}	2.1×10^{0}
100	240.0	6×10^{-4}	8.6×10^{-10}	2.3×10^{13}	9.5×10^{0}
110	270.0	2×10^{-4}	2.0×10^{-10}	7.4×10^{12}	3.8×10^{1}
120	330.0	6×10^{-5}	5.6×10^{-11}	2.7×10^{12}	1.3×10^{2}
130	390.0	2×10^{-5}	1.9×10^{-11}	1.2×10^{12}	3.7×10^{2}
140	447.0	7×10^{-6}	7.6×10^{-12}	1.7×10^{11}	8.7×10^{2}
150	503.0	3.7×10^{-6}	3.4×10^{-12}	7.4×10^{10}	1.8×10^{3}
160	560.0	2×10^{-6}	1.6×10^{-12}	...	3.6×10^{3}
180	676.9	7×10^{-7}	4.8×10^{-13}	...	1.0×10^{4}
200	792.5	3×10^{-7}	1.7×10^{-13}	...	3.0×10^{4}
220	906.6	1.4×10^{-7}	7.0×10^{-14}	...	8.7×10^{4}

[a] *Phys. Rev.*, **88**, 1027 (1952); *Mon. Not. Roy. Astron. Soc.*, **112**, 101 (1952).

values together with temperatures are listed in Table 3. The mean free path has the same meaning in upper air research as used by chemists. It is not the distance between the particles as some recent statements would imply, but the average distance a particle travels between collisions with other particles. At an altitude of 800 miles this value is about 2000 miles, while the average distance between the particles is only 0.0076 cm. This parameter is of importance in sound-wave propagation and hence in temperature measurements at high altitudes.

Temperatures of the Upper Atmosphere. At altitudes of the upper atmosphere the concept of temperature takes on a somewhat different meaning than we usually understand it on the surface of the earth. There is a popular misconception that the high temperatures encountered at high altitudes will cause missiles to melt. The temperature in the upper atmosphere is called the kinetic temperature of the atmospheric particles. It is determined from the mean kinetic energy of the particles and is independent of density. Since the density of the particles is extremely low and the mean free path extremely large the effect of the particles on the temperature at these altitudes is relatively slight. The temperature of the body is determined almost entirely by radiation energy. This exchange process is very slow in the upper atmosphere, making the conventional thermometer unsuitable for high-altitude temperature measurements.

Prior to about seven years ago our information on the physical and chemical states of the upper atmosphere, its pressure, temperature, density, and composition, were deduced from observations near the earth's surface and from low-altitude balloon ascents. Since 1946 extensive upper-air measurements of these parameters have been made by the use of V-2's, Vikings, and Aerobee rockets (see Figures 3 and 4). As a result, many new fundamental data have been obtained. Up to the present time no method has been developed for the direct measurement of temperature in the upper atmosphere by rockets. Hence temperature must always be deduced from such parameters as pressure, density, or the velocity of sound involving the Mach number determination. (The Mach number is the ratio of the

Courtesy of The Glenn L. Martin Co., Baltimore 3, Maryland

Figure 3. Viking No. 9 Taking Off from the Launching Stand

The white cloud at the right is steam from water in the pit beneath the launching stand. The water is vaporized by the tremendous heat from the rocket engine. The altitude record for single-stage rockets is 135.6 miles. A WAC Corporal launched from the nose of a German V-2 in a two-stage operation attained about 250 miles.

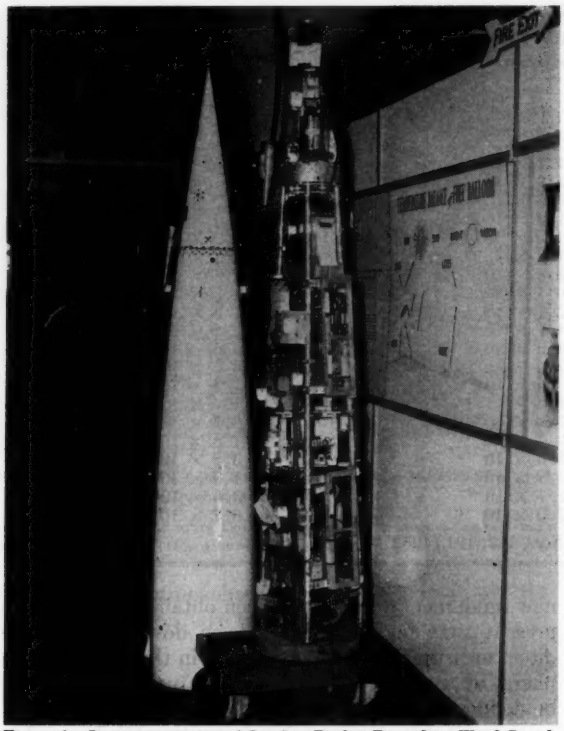


Figure 4. Instrumentation of Aerobee Rocket Recording Wind Speed, Pressures, Temperature, and Relative Humidity

The instrumentation is enclosed in the nose of the rocket which is blown off at the top of the flight. Measurements are telemetered (radioed) to ground stations during flight.

speed of flight of the rocket to the speed of sound.) There is an area on each rocket, usually just in front of the tail fins, where ambient pressure exists during flight.

For low altitudes (below 110 km.) the density ρ of the atmosphere is calculated from the following relationship derived from Rayleigh's formula, modified for rocket velocities greater than the velocity of sound. The ratio of specific heats of air is set equal to 1.4.

$$\rho = 0.144 \frac{P}{V^2} - \frac{0.066}{V^2} p + \ldots$$

where ρ is the ambient density, P is the ram, or stagnation, pressure measured at the nose of a yawless supersonic rocket, V is the velocity of the rocket, and p is the ambient pressure.

At high altitudes, above 110 km., the mean free path becomes comparable to the size of the rocket. In this case densities are determined from the following formula which is derived from kinetic theory:

$$\rho = \frac{0.182\ \Delta P}{V_1} \quad [g.\ m.^{-3};\ \text{mm. Hg};\ \text{km. sec}^{-1}]$$

where ΔP is the total change in pressure, during one roll, in a gage on the side of a rolling rocket, V_1 is the rocket velocity normal to the gage opening, and ρ is again the ambient density. The following relationship obtains for the relation of temperature, pressure, and height:

$$T = \frac{485\ p}{\rho}$$

$$dp = -7.5\ \rho\ g\ dh$$

where p is given in mm. of Hg, T in degrees Kelvin, ρ in g./m.^{3}, g in km./sec^2, and h in km.

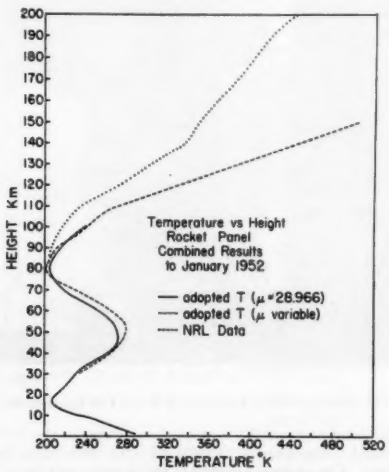


Figure 5. Temperature Distribution Data [*Phys. Rev.*, 88, 1027–32 (1952)]

TABLE 4
Composition of the Atmosphere (Dry) Up to About 60 km.

Constituent	*Per cent by volume*	*Reduced thickness atmo-cm. NTP*[a]
Nitrogen	78.09	625,000
Oxygen	20.95	168,000
Argon	0.93	7,440
Carbon dioxide	0.03	240
Neon	1.8×10^{-3}	14.6
Helium	5.24×10^{-4}	4.2
Krypton	1×10^{-4}	0.8
Hydrogen	5×10^{-5}	0.4
Xenon	8×10^{-6}	0.06
Radon	6×10^{-18}	(variable decreasing with height)

[a] The total amount of any constituent of the atmosphere may be indicated by giving the thickness of the layer formed if the constituent were separated out and spread over the base of the column at NTP. The amount may be expressed in atmo-units—atmo-cm., atmo-mm., or atmo-km.

It should be emphasized that above 160 km. the temperatures and densities become highly uncertain. The NRL (Naval Research Laboratory) obtained a value of $\rho = 1.0 \times 10^{-13}$ g./cm.^{3} at a height of 219 km. for the density from a rocket flight on August 7, 1951.

In view of the great interest in knowing the temperature at high altitudes the Geophysics Research Directorate, U. S. Air Force Cambridge Research Center, coordinated four independent methods for determining temperatures of the upper atmosphere simultaneously over the Tularosa Basin, New Mexico. This project

was known as "*T*-Day," or Temperature Day, October 22, 1952. Basically, the methods were air density, sound velocity, and aerodynamic techniques. Briefly, the experiments were designed to determine temperatures and winds up to about 115 km. (70 miles) above the earth's surface. The four methods were: (*a*) photographing meteor trails to measure the rate of deceleration and change in brightness (providing an indication of the density of the atmosphere, from which temperature may be derived); (*b*) density determinations from rocket flights; (*c*) a sonic method from ground explosions of TNT (in which the refraction of the resulting sound waves generated from the explosion was recorded by several widely separated listening stations); (*d*) a searchlight technique employing two 60-inch antiaircraft searchlights stationed on adjacent mountain tops. One of the searchlights served as a transmitter sending a high-intensity beam of light into the sky. The light was flashed on and off at a fixed frequency. The second searchlight was a receiver equipped with a very sensitive photomultiplier tube and tuned to respond to the frequency of the transmitter. Light scattering by the atmosphere depends on the density of the air. From the intensity of the light received the density of the air, and hence temperature values, are calculated.

In Figure 5 is shown the basic temperature data compiled by the Upper Atmosphere Rocket Research Panel. These are probably the best current results on temperatures in the upper atmosphere. They represent the averaged results of the Naval Research Laboratory (NRL), the Signal Corps Electronic Laboratory (SCEL), the University of Michigan Air Force, and the University of Michigan Signal Corps.

From the figure it may be observed that the temperature of the atmosphere at first decreases with height, reaching a minimum at about 20 km. Above this height the temperature rises, attaining a maximum at about 50 km. In this region the temperature may even exceed that on the surface of the earth. This increase in temperature is ascribed to the absorption of solar ultraviolet radiation by the ozone layer. At an altitude above the ozone layer the temperature again decreases to a minimum at about the 80 km. level. At greater altitudes the temperature rises to extremely high values with a probable maximum of 1500 to 3000°K. at the "critical level" (400–500 km.). However, there are many conflicting views, with different estimates for temperatures at higher altitudes.

For evaluating temperatures at extremely high altitudes various theoretical deductions from radiation equilibrium, spectroscopic observations of the night airglow and aurorae, and ionospheric parameters are employed. The latter method involves calculations from collisional frequencies, recombination coefficients, ionospheric scale height, diurnal and nocturnal variation in electron concentration, and seasonal and latitudinal variations in the solar zenith angle.

TABLE 5
Minor Constituents of the Atmosphere

Constituent	*Per cent by volume*	*Reduced thickness, atmo-cm. NTP*	*Reference*
Water vapor	0.1–2.8	0.25–50 mm., liquid water	LANDOLT-BORNSTEIN, "Astronomie und Geophysik," 1952, Vol. III, p. 568.
Ozone	1×10^{-6}	0.3	*Centen. Proc. Roy. Meteorol. Soc.*, 1950, 5–8.
Nitrous oxide	5×10^{-5}	0.4	*Phys. Rev.*, 78, 65 (1950); *Proc. Am. Phil. Soc.*, 93, 372 (1949).
Methane	1.4×10^{-4}	1.2	*Proc. Am. Phil. Soc.* 93, 372 (1949).
Carbon monoxide	1×10^{-4}	0.09–0.5	*Phys. Rev.*, 87, 380 (1952); *ibid.*, 85, 481 (1952).
Heavy water	10^{-6} of water vapor		.....

TABLE 6
Constitution of the Upper Atmosphere[a]

Constituent	*70 km.*	*95 km.*
O	10^{11} atoms/cm.^{3}	10^{12}
O_2	10^9 molecules/cm.^{3}	10^8
H_2O	10^{10} molecules/cm.^{3}	10^5
OH	10^8 molecules/cm.^{3}	10^3
H	10^9 atoms/cm.^{3}	10^9
Na	10^4 atoms/cm.^{3}	3
N_e	10^3 electrons/cm.^{3}	5×10^4
Total particle concentration	2.5×10^{15}/cm.^{3}	10^{13}

[a] From theoretical calculations by Bates and Nicolet.

COMPOSITION

The composition of the air in the troposphere and stratosphere is well known from direct analysis by chemical methods upon samples collected by balloon ascents, and more recently from Aerobee rockets. There is no change in composition up to a height of about 60 km. The most reliable data are the values given in Table 4 by F. A. Paneth (*9*). Since the amount of water vapor in the atmosphere is variable the values are given for dry air.

It is surprising to note that geophysicists and investigators in upper-air research are interested mostly in the minor constituents of the atmosphere, as ozone, nitrous oxide, methane, carbon monoxide, atomic oxygen, and neutral sodium atoms. In Tables 5 and 6 the amounts of these minor constituents are listed. Their abundance is relatively minute but important. The values are usually expressed in atmo-cm. (or atmo-mm.) and also in the number density, which are useful quantities in upper atmospheric research.

One might well raise the question why it is of such great interest to study the abundance and vertical distribution of such rare atmospheric constituents which comprise less than one-millionth of the atmosphere. Evidence has been obtained that weather conditions in the troposphere, and hence on the earth's

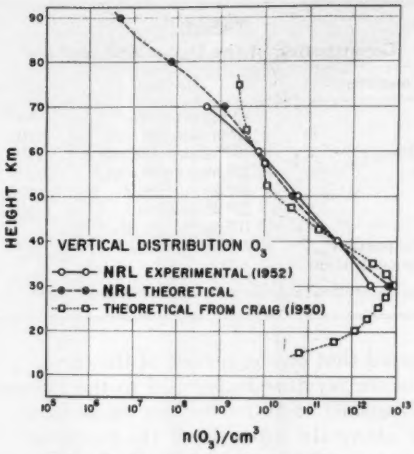


Figure 6. Vertical Distribution of Ozone

surface, are directly associated with physical and chemical conditions at altitudes of tens and even of hundreds of kilometers.

It is well known that ozone absorbs very strongly ultraviolet radiation of wave length below 2900 Å., and therefore cuts off all solar radiation of shorter wave length. Infrared radiation from the surface of the earth is absorbed by ozone, water vapor, carbon dioxide, and nitrous oxide. Also, the atmosphere loses energy by infrared emission of these gases. These minor constituents have intense and complex absorption spectra. If the abundance and vertical distribution, along with the absorption coefficients, are known, these data should make it possible to calculate the atmospheric temperature gradient. These radiative processes are the source and sink of the irreversible heat engine which is our atmosphere. In addition, these minor constituents are subject to various photochemical effects produced by absorption of the solar ultraviolet, effects which are of economic consequence and of beneficial physiological protection.

OZONE

The first quantitative studies of ozone in the upper levels of the atmosphere were made by Fabry and Buisson in 1921 (*10*). Although there are only traces of ozone in the upper atmosphere, equivalent to 3 mm. NTP, this small amount is sufficient to intercept all solar radiation below λ 2900 Å. It is therefore of greatest importance in controlling the ultraviolet radiation in a spectral region distinguished by a number of biological effects, *e. g.*, vitamin D formation, erythema, and bactericidal action. There exists a fairly well established correlation between the amount of atmospheric ozone and meteorological conditions.

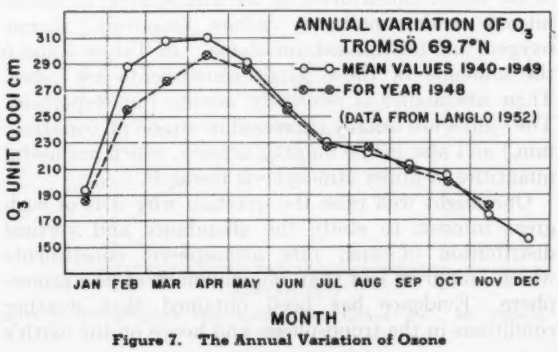

ANNUAL VARIATION OF O_3
TROMSÖ 69.7°N
MEAN VALUES 1940-1949
FOR YEAR 1948
(DATA FROM LANGLO 1952)
O_3 UNIT 0.001 cm
JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC
MONTH

Figure 7. The Annual Variation of Ozone

The basic principle for determining the amount of ozone in the atmosphere is the spectrographic measurement of the relative intensity of the solar spectrum. Since the ultraviolet absorption by ozone increases in intensity at about 3300 Å. and reaches a maximum at about 2500 Å., by measuring the intensity at two different wave lengths on the long wave length side of this absorption band it is possible to deduce the amount of ozone through which the light has passed and consequently the ozone concentration above the location of observation. Photomultiplier tubes have a low "signal/noise ratio" and permit measurements to be made of much weaker light than the photoelectric instruments used prior to the war. With these more recent methods the vertical distribution of ozone can be obtained with greater precision by photographing the solar spectrum at great heights.

TABLE 7
Distribution of Ozone with Height in Three Different Layers

O_3 unit 0.001 atmo-cm. layer	*Total amount of ozone Tromsoe 69.7°N.*				
	160	*220*	*280*	*340*	*400*
50–35 km.	18	13	16	20	18
35–20 km.	112	155	180	187	192
20–0 km.	30	52	84	133	190

Direct measurements of the vertical distribution of atmospheric ozone to 70 km. altitude have been accomplished by workers at NRL (*11*) over White Sands Proving Grounds, New Mexico. The data were obtained by photographing the ultraviolet spectrum of the sun with two small spectrographs installed in an Aerobee rocket. After retrieving these instruments with the films and records the vertical distribution of atmospheric ozone was estimated. Figure 6 shows graphically their data, as well as calculated data from photochemical theory by Craig (*12*). The maximum concentration was found to occur between 18 and 30 km. The ozone concentration above 35 km. appears to decrease approximately exponentially with increasing altitude. The measurements were made to a height of 70 km., which was the highest altitude at which ozone was definitely detected.

It is interesting to note that there are seasonal and latitudinal variations in the amount of ozone. There is more ozone in high latitudes than in low. Atmospheric ozone has a well established annual cycle with a maximum in spring and a minimum in autumn in

both hemispheres. The distribution of ozone with height in the atmosphere for different total amounts of ozone is shown in Table 7. The values are given as the amount present in three different layers from data of Langlo (*13*). The annual variation is shown in Figure 7.

The photochemical theory of ozone formation was first discussed by Chapman in 1930 (*14*). The photochemical dissociation of molecular oxygen has been studied by a number of investigators (*15*, *16*, *17*, *18*). In the weak Herzberg continuum beginning at $\lambda < 2425$ Å. molecular oxygen is dissociated according to the following process:[3]

$$O_2 + h\nu \xrightarrow{\lambda < 2425 \text{ Å.}} 2\,O\,(^3P)$$

The atoms of atomic oxygen thus liberated in the presence of a third body may unite with oxygen molecules to form ozone.

$$O_2 + O + M \rightarrow O_3 + M$$

The ozone is destroyed by absorption in the strong Hartley continuum (λ 3509–2100 Å.).

$$O_3 + h\nu \xrightarrow{\lambda < 3500 \text{ Å.}} O_2 + O\,(^1D)$$

Ozone is also photodissociated in the visible in the weak Chappuis continuum (λ 8000–6000 Å.).

$$O_3 + h\nu \rightarrow O_2 + O\,(^3P)$$

The following collisions may also occur as secondary reactions.

$$\begin{aligned} O + O + M &\rightarrow O_2 + M \\ O + O_3 &\rightarrow 2O_2 \\ O_3 + O_3 &\rightarrow 3O_2 \end{aligned}$$

From these reactions the vertical distribution of atmospheric ozone has been obtained through theoretical photochemical calculations involving such factors as (*a*) emission spectrum of the sun in the ultraviolet, (*b*) the absorption spectra of oxygen and ozone, (*c*) coefficients of collision, and (*d*) the vertical distribution of oxygen and nitrogen.

ATOMIC OXYGEN

There is abundant evidence from the spectra of the night airglow and the aurorae that atomic oxygen is a permanent constituent in the higher atmosphere. The green auroral line λ 5577.35 Å. is the strongest line in the spectrum of the night airglow. This radiation has been identified as a forbidden transition of O I[4] (^1S–^1D). The red oxygen lines λ 6300 Å. and λ 6363 Å. are also prominent features of the night sky radiation.

Molecular oxygen is readily dissociated by solar radiation, as seen in the photochemical mechanism for ozone. Very strong absorption by oxygen occurs above an altitude of about 80 km. Here absorption in the Schumann-Runge absorption bands (λ 1925–1760 Å.) produces atomic oxygen by the following process:

$$O_2 + h\nu \xrightarrow{\lambda < 1759 \text{ Å.}} O\,(^3P) + O\,(^1D)$$

The oxygen atoms may recombine either in a two-body, or a three-body collision process.

$$\begin{aligned} O + O + M &\rightarrow O_2 + M \\ O + O &\rightarrow O_2 + h\nu \end{aligned}$$

In general, the three-body association process occurs at a slower rate than the two-body process. By considering recombination rates, recombination coefficients, and recombination cross sections, the vertical distribution of atomic oxygen and oxygen molecules has been calculated theoretically by Penndorf (*19*, *20*), Moses and Wu (*21*), Nicolet (*22*), Choudling (*23*), and others. According to Penndorf the dissociation of molecular oxygen into atomic oxygen becomes appreciable at a height of about 95 km. and is almost complete above 125 km. Figures 8 and 9 show the vertical distribution of atomic and molecular oxygen.

ATOMIC NITROGEN

The question as to the state of nitrogen in the upper atmosphere is still uncertain. Photodissociation is much more difficult to achieve for molecular nitrogen than for molecular oxygen. Nitrogen is more readily ionized than dissociated, at least by sunlight. Radiations shorter than λ 750 Å. are required to photodissociate nitrogen while radiation at 2000 Å. can dissociate oxygen. The absence of N I emissions in the night airglow, and the presence of N_2^+ emissions very high in sunlit aurorae have been the chief reasons for assuming that nitrogen in the upper atmosphere is

TABLE 8

Electronic Configurations and Term Symbols for the Deeper Energy Levels of O, O^+ and O^-

	Configuration	*Term*	*Remarks*
Neutral atom, O	$(1s)^2\,(2s)^2\,(2p)^4$	^3P	Ground term, ionization potential 13.55 e. v.
		^1D	Metastable term, 1.96 e. v. above ^3P.
		^1S	Metastable term, 4.17 e. v. above ^3P.
	$(1s)^2\,(2s)^2\,(2p)^3\,3s$	$^5S^o$	9.10 e. v. above ^3P.
Positive ion, O^+	$(1s)^2\,(2s)^2\,(2p)^3$	$^4S^o$	Ground term, ionization potential 34.93 e. v.
		$^2D^o$	Metastable term, 3.31 e. v. above $^4S^o$.
		$^2P^o$	Metastable term, 4.99 e. v. above $^4S^o$.
	$(1s)^2\,(2s)\,(2p)^4$	^4P	14.78 e. v. above $^4S^o$.
Negative ion, O^-	$(1s)^2\,(2s)^2\,(2p)^5$	$^2P^o$	Ground term, detachment potential 2.2 e. v.
	$(1s)^2\,(2s)^2\,(2p)^4\,3s$	^4P ^2P	The energies of these terms are not known with certainty, but they may be nearly equal to that of the gound level of O.
	$(1s)^2\,(2s)\,(2p)^6$	^2S	

From Massey, H. S. W., and D. R. Bates, *Repts. Progr. in Phys.*, **9**, 63 (1942–43).

[3] The relation of the Term Symbols to the conventional electronic configurations is shown in Table 8.

[4] The symbols O I, O II, O III, N I, etc., represent neutral atomic oxygen, O^+, O^{++}, N, etc., and are commonly used in spectroscopy.

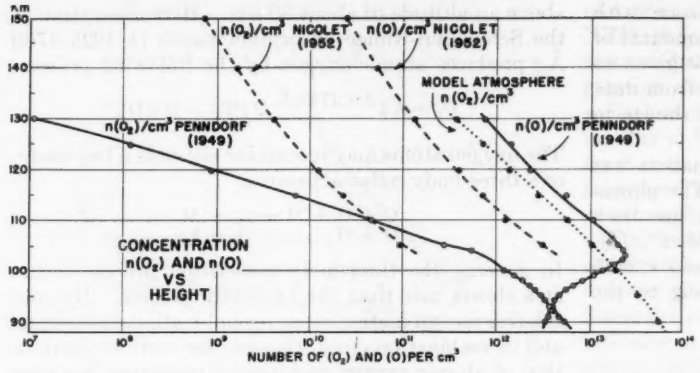


Figure 8. The Vertical Distribution of Atomic and Molecular Oxygen in the Upper Atmosphere

The very strong absorption of ultraviolet radiation by molecular oxygen in the Schumann-Runge region of the spectrum occurs at altitudes above about 80 km. Dissociation is practically complete at the 120–130 km. level.

mainly in the molecular state. The absence of the N I lines, however, is not definite. A theoretical discussion of the state of nitrogen in the upper atmosphere by Deb (*24*) and Nicolet and Pastiels (*25*) probably gives the latest information on the topic of atomic nitrogen. The forbidden lines of N I, λ 2466 (^2P–^4S) and λ 5198 (^2D–^4S) in the auroral spectrum, give definite evidence of the presence of atomic nitrogen at least in the auroral region.

DISTRIBUTION OF SODIUM

The announcement that neutral sodium occurs in the upper atmosphere must certainly appear anomalous, remembering from freshman chemistry its extreme activity in the presence of even traces of water. The definite identification of neutral sodium as a permanent constituent of the atmosphere was established from spectroscopic observations of the twilight and night luminescence of the sky. Figure 10 shows the vertical distribution and Figure 11 the annual variation, while Figure 12 is a spectrogram of the twilight luminescence showing the enhancement of λ 5893 Å. band of sodium.

The emission heights of λ 5893 Å. radiation were first calculated to be from 60 to 80 km. from observations of the twilight enhancement. Later work at Cactus Peak, California, and at College, Alaska, by Elvey (*26*), Roach, Barbier, and Pettit (*27, 28, 29, 30*) from studies of the night airglow indicates the emission range to be 200 to 600 km. with a mean value of approximately 220 to 300 km.

The theory of Chapman (1939) has found general provisional acceptance in explaining the mechanism of emission in the night airglow. At levels where there is

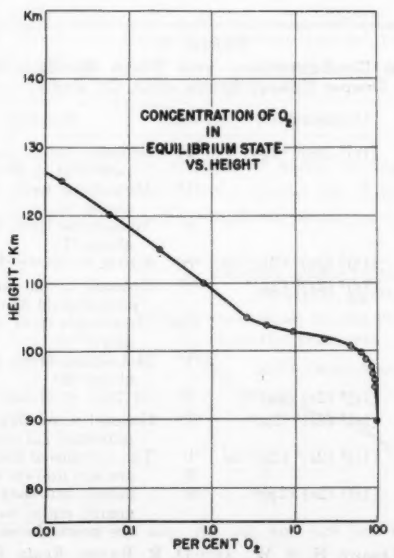


Figure 9. Variation of the Concentration of Molecular Oxygen with Height from Data of Penndorf

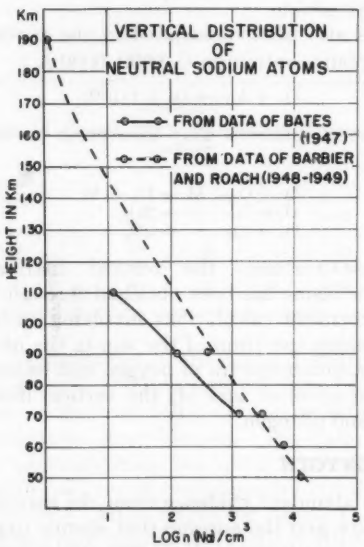

Km
VERTICAL DISTRIBUTION OF NEUTRAL SODIUM ATOMS
FROM DATA OF BATES (1947)
FROM DATA OF BARBIER AND ROACH (1948-1949)
HEIGHT IN Km
LOG n (Na) /cm3

Figure 10

an abundance of free oxygen atoms the following reactions may occur.

$$Na + O + M \rightarrow NaO + M$$

(M represents any third body necessary for a third-body collision—probably O_2, O, and N_2 particles.) The free sodium may be formed again by the reaction of sodium oxide with atomic oxygen.

$$NaO + O \rightarrow Na^* \text{ (excited)} + O_2$$
$$Na^* \rightarrow Na + h\nu\ (\lambda\ 5893)$$

The excitation energy of the ^2P level of sodium is 2.10 volts. The source of this energy is considered to come

from the energy stored in atomic oxygen atoms as a result of dissociation of molecular oxygen by sunlight during the day.

NITROUS OXIDE

The presence of nitrous oxide (N_2O) as a world-wide permanent constituent in the earth's atmosphere was first observed by Adel (*31*) from infrared spectroscopic evidence of the ν_1 fundamental at 7.8 μ in the solar spectrum. Later the presence of atmospheric nitrous oxide was confirmed by observational bands at 3.9 μ, 4.5 μ, and 8.6 μ by Migeotte (1949); and by Shaw, Sutherland, and Wormell (1948) through recognition of bands at 3.9 μ, 4.1 μ, and 4.5 μ.

The abundance of atmospheric nitrous oxide was determined by McMath and Goldberg (*32*) by comparing the intensities of the lines of the 2.13 μ band in the solar spectrum with that produced by a known amount of nitrous oxide in the laboratory (see Figure 13). The telluric absorption was found to be equivalent to that which would be produced by 4 mm. of nitrous oxide at NTP. The molecular abundance has been estimated to be about 2×10^{19}/cm.^{2} column. It is, therefore, more abundant than ozone. From radiation temperature measurements of the atmospheric nitrous oxide by Adel (*33*), together with the distribution of rotational intensities displayed by the atmospheric bands, the nitrous oxide layer in the atmosphere appears to be largely in the troposphere.

METHANE AND CARBON MONOXIDE

The distribution of methane in the earth's atmosphere appears to be world-wide in character. It has been observed at an altitude of 6000 feet at Mount Wilson Observatory. Its density falls off exponentially with height, following the same rate as the main body of the atmosphere. The abundance has been measured by Goldberg (*34*). The total quantity of methane in the earth's atmosphere has been estimated to be equivalent to that which would be contained in a layer 1.2 cm. thick at NTP. The molecular concentration is of the order of 2.09×10^{19} in a vertical column of air of 1 sq. cm. cross section.

Atmospheric carbon monoxide has recently been reported from several localities by Adel (*35*), Shaw and Howard (*36*), and Migeotte and Neven (*37*). Its presence has been observed in the atmosphere over Flagstaff, Arizona; Columbus, Ohio; and at the International Research Station at the Jungfraujoch, Switzerland. The abundance over Columbus, Ohio, has been determined to be 0.09 atmo-cm. Evidence seems to be accumulating that atmospheric carbon monoxide is planet-wide.

WATER VAPOR

Water vapor in the atmosphere absorbs most of the infrared radiation of the sun. Prior to World War II

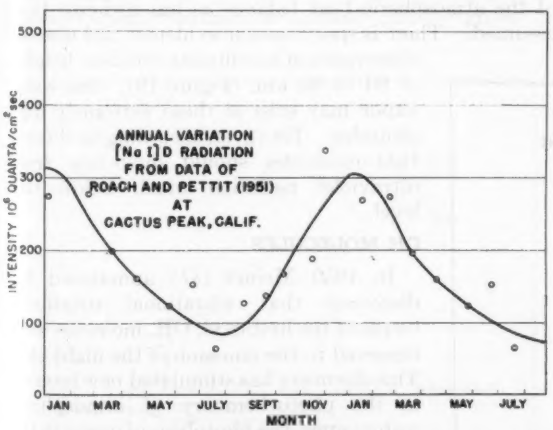
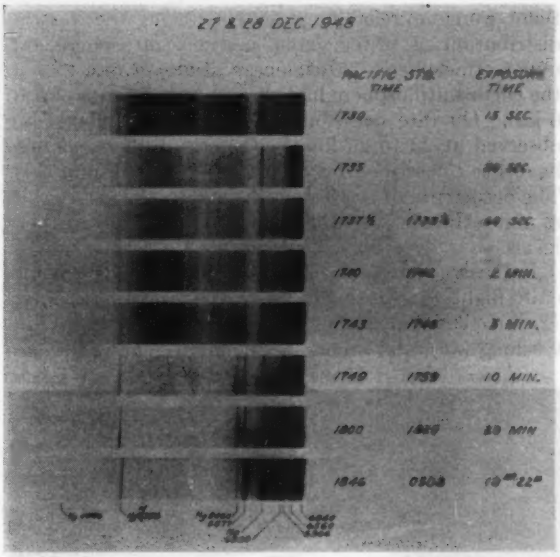


Figure 11. The Annual Variation in the Intensity of the Sodium D 5893 Å. Radiation

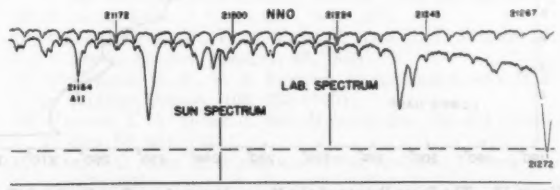
There is a maximum intensity during winter and a minimum during summer in the Northern Hemisphere, a maximum during winter and a minimum during summer in the Southern Hemisphere. Thus the southern is six months out of phase with the northern.



Courtesy of Dr. C. T. Elvey of the Geophysical Institute, University of Alaska

Figure 12. Spectrogram of the Twilight Luminescence of the Night Sky Showing the Enhancement of λ 5893 Å. Band of Sodium

It may be observed that at 1743 hours the intensity is most pronounced while a few minutes afterward the intensity of the line is greatly diminished.



Courtesy of Dr. Robert R. McMath and Dr. Leo Goldberg of the McMath-Hulbert Observatory, University of Michigan

Figure 13. A Comparison of the Absorption Band of Atmospheric Nitrous Oxide in the Solar Spectrum with a Laboratory Spectrum

there were no reliable measurements of the vertical distribution of water vapor in the stratosphere and upper atmosphere. Most observations of moisture in the earth's atmosphere have been below heights of 5 to 6 km. On rare occasions mother-of-pearl clouds are observed at 22 to 29 km. in the stratosphere. These have been described by Störmer (*38*) (see Figure 14). The occurrence of these clouds is taken as evidence that at times the air is saturated with water vapor at these levels.

Extensive determinations of water vapor from aircraft flights just into the lower stratosphere at about 12 km. have been made by Dobson, Brewer, and Cwilong (*39*), and others in England. The results are shown in Figures 15 and 16. Barrett and co-workers (*40*) have extended water vapor measurements to an altitude of about 32 km. from radiosonde balloon ascents. These were carried out in cooperation with the U. S. Navy under Project Skyhook. Their results are shown in Figures 17 and 18. One important and significant observation made from these soundings was the marked increase in mixing ratios between the 16 and 30-km. region. In one case the mixing ratio at 30 km. was more than 20 times the mixing ratio at 17 km.

Courtesy of Professor Carl Störmer, Institute for Theoretical Astrophysics, Blindern, Oslo, Norway

Figure 14. Mother-of-Pearl Clouds

Photographed by Professor Störmer on February 1, 1932, at about 8 A.M. The clouds were about 23 km. high, and consisted of streams of small flocculi, each shining in a series of different colors.

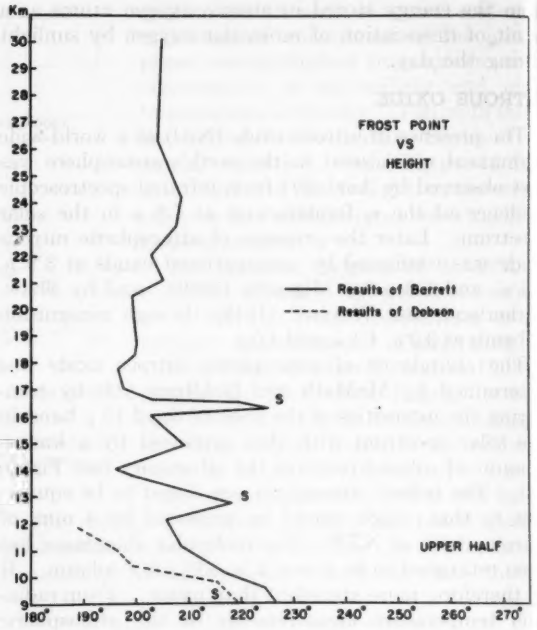


Figure 16. Continuation of Figure 15

The data reported from these observations indicate that the concentration of water vapor at these altitudes is not small enough to be neglected in studies of the atmospheric heat balance as has hitherto been assumed. There is spectroscopic evidence, and also the observance of noctilucent clouds at heights of 80 to 90 km. (Figure 19), that water vapor may exist at these extremely high altitudes. However, according to theory, H_2O molecules should dissociate from ultraviolet radiation much below this level.

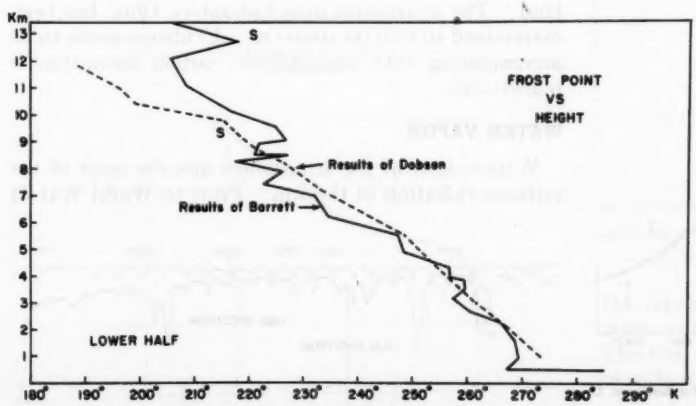


Figure 15. The Frost Points of the Upper Atmosphere Over England (Results of Dobson) and Camp Ripley, Minnesota (Results of Barrett)

Note the sharp change of the fall of the frost points on entering the stratosphere. There is a second saturation point in the middle stratosphere over Camp Ripley.

OH MOLECULES

In 1950 Meinel (*41*) announced his discovery that vibrational rotational bands of the hydroxyl, OH, molecule were observed in the emission of the night sky. This discovery has stimulated new interest in the photochemistry of atmospheric water vapor, the photolysis of ozone in the presence of water vapor, and spectrographic and radiation studies of water vapor. Roach, Pettit, and Williams (*42*), and Bates and Nicolet (*43*) have made extensive theoretical studies on the photol-

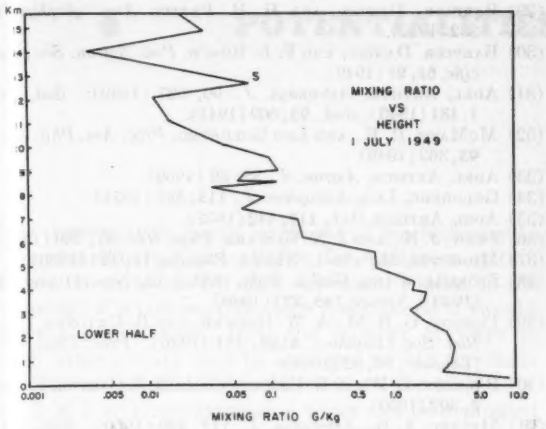


Figure 17. Variation of Mixing Ratio with Altitude in the Stratosphere (from Results of Barrett and Others)

Mixing ratio is defined as M_v/M_a, where M_v is the mass of water vapor and M_a is the mass of dry air.

ysis of atmospheric water vapor and the OH molecule. The height of the emission layer of the OH molecules was calculated to be about 70 km.

CONCLUSION

Even a brief survey of the literature will serve to emphasize the complexity of the upper regions of the terrestrial atmosphere. As yet only a limited amount of direct data from balloon and rocket flights has been collected. There are many intriguing and challenging topics for study in upper atmospheric research which are vital to chemistry, and many uncertainties and conflicting statements, which in order to be resolved, will require much additional information. Although much progress has been made in understanding the upper atmosphere, the questions and problems yet unsolved greatly outnumber answers already given.

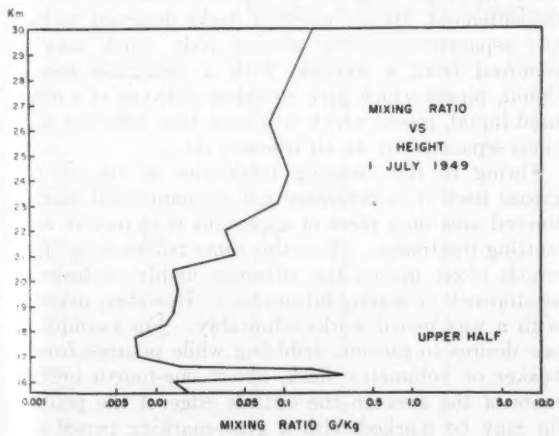


Figure 18. Continuation of Figure 17

Note that in this sounding the mixing ratio at the 30 km. level is about 20 times that at 17 km.

Courtesy of Professor Carl Störmer, Institute for Theoretical Astrophysics, Blindern, Oslo, Norway

Figure 19. Noctilucent Clouds (Luminous Night-Clouds)

The picture was taken on the night between July 27 and 28, 1909, at 11:01 P.M., by Professor Störmer, at his summer residence, Villa X, near the town of Drobak, 30 km. (18.6 miles) south of Oslo. The outline of the Island Haaoen is seen in the background. The mean height of the clouds was 81.4 km. (50.5 miles). The occurrence of these clouds is taken as evidence that water vapor occurs at these extreme altitudes in the upper atmosphere.

TABLE 9

Volume Per Cent of Water Vapor in the Atmosphere[a]

	North latitude								
	80	*70*	*60*	*50*	*40*	*30*	*20*	*10*	*0*
Jan.	0.009	0.1	0.2	0.4	0.7	1.3	1.8	2.5	2.8
July	0.5	0.9	1.2	1.4	1.8	2.3	2.5	2.7	2.8
	South latitude								
Jan.			0.5	0.8	1.4	2.0	2.3	2.6	2.8
July			0.5	0.6	1.0	1.4	1.7	2.3	2.8

[a] Data from R. PENNDORF in LANDOLT-BORNSTEIN, "Astronomie und Geophysik," **1952**, Vol. III, p. 568.

ACKNOWLEDGMENT

This will acknowledge with appreciation the helpful criticisms of Dr. R. Penndorf of the Geophysics Research Directorate, AFCRC, who read the manuscript, for his numerous discussions and valuable suggestions for its revision.

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TWO EFFECTIVE BUT INEXPENSIVE ANTIWETTING AGENTS

JAY E. TAYLOR
Ohio State University, Columbus, Ohio

THE capacity of the silicones to confer antiwetting and anticreeping properties upon glass is well known. Certain rather costly preparations of selected silicone derivatives are on the market for these uses. An inexpensive and yet excellent antiwetting agent may be easily prepared from ordinary silicone grease.

Approximately one gram of either regular or vacuum silicone grease is dissolved completely in 50 ml. of low-boiling petroleum ether or similar solvent. Vigorous shaking is necessary. If regular silicone grease is used the resulting cloudy solution may be filtered and the clear filtrate used immediately. If the vacuum grease is used it will be necessary to allow the mixture to stand for about one week and then decant the clear solution from the settled precipitate. The glass surface to be treated is first carefully cleaned and dried. Following this, it is rinsed with clear silicone solution, allowed to drain, thoroughly dried either in an oven or by long standing, and finally treated with cleaning solution and rinsed to smooth the surface. A surface coated in this manner will withstand several subsequent treatments by cleaning solution with only a moderate loss in antiwetting efficiency.

This preparation has been used in this laboratory with excellent success on a variety of articles. These have included beakers to contain solutions for pH measurement, special reaction flasks designed to hold two separate solutions, stirring rods which may be removed from a solution with a negligible loss of liquid, pipets which give complete delivery of a measured liquid, pipets which will hold two different solutions separated by an air column, etc.

Owing to the creeping tendencies of the silicone grease itself it is definitely not recommended when a limited area on a piece of apparatus is to receive antiwetting treatment. (It is this same tendency to creep which often makes the silicones highly undesirable as stopcock or sealing lubricants.) However, marking with a wax pencil works admirably. For example, if one desires to prevent dribbling while pouring from a beaker or volumetric flask, about one-fourth inch or more of the area on the outside edge of the pouring lip may be marked with a glass-marking pencil and then warmed to melt or sinter the wax. This gives a highly effective antiwetting surface which will not spread beyond the area of application.

POTENTIALITIES OF PROTEIN ISOMERISM

ISAAC ASIMOV
Boston University School of Medicine, Boston, Massachusetts

It is customary in many textbooks of biochemistry to emphasize the vast potentiality for isomerism within the protein molecule by some statement similar to the following: if a polypeptide chain is composed of twenty different amino acids, then the number of ways in which those twenty may be arranged within the chain is 20! (*i. e.*, "factorial 20" or $20 \times 19 \times 18 \times 17 \times \ldots \times 4 \times 3 \times 2 \times 1$), an expression which can be evaluated as 2.43×10^{18}. Leathes[1] goes further, assuming a chain of 50 amino acids of 19 different kinds, one occurring 10 times, four occurring four times, 10 occurring twice, and the remainder once each. The number of possible permutations is thus given by him as 10^{48}.

These are large numbers and impressive ones, but such examples suffer from the very fact of their artificiality. The potentialities of isomerism could be brought home with greater force if cases of actual protein molecules of which the amino acid composition were known, were taken into consideration.

The amino acid composition of eleven proteins is presented in Table 1, the data being derived from several sources.[2, 3, 4] For purposes of computation, it is necessary to make certain minor modifications in the data as given. Thus, where amide groups are reported without definite identification as asparagine or glutamine, they were arbitrarily assigned to the available aspartic acid and glutamic acid as equally as possible. Figures for "half-cystine" molecules were divided by two in order to obtain values for cystine itself. Where a fractional value for the number of residues of a particular amino acid within a molecule is given, the nearest whole number was taken. None of these modifications significantly affects the general conclusions to be drawn.

Let us assume for purposes of argument that each of the proteins named in Table 1 is composed of a single polypeptide chain consisting of the stated numbers of the various amino acids listed, these amino acids occurring in some unknown order along the chain. If there are n amino acids in the chain, of which a are of one type, b of another, c of another, etc., the number of different polypeptide chains that can be built of them by altering the order of occurrence is:

$$\frac{n!}{a! \times b! \times c! \times d! \times \ldots} \qquad (1)$$

To take salmine as an example (see Table 1), formula 1 would become:

$$\frac{58!}{40! \times 7! \times 4! \times 3! \times 2! \times 1! \times 1!} \qquad (2)$$

[1] Leathes, J. B., *Science*, **64**, 387 (1926).
[2] Tristram, G. G., *Advances in Protein Chem.*, **5**, 84 (1949).
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TABLE 1
Number of Amino Acid Residues per Molecule in Various Proteins

	Salmine	*Insulin*	*Ribonuclease*	*Horse myoglobin*	*Pepsin*	*Chymotrypsin*	*β-Lactoglobulin*	*Silk fibroin*	*Ovalbumin*	*Edestin*	*Horse hemoglobin*
Glycine	3	7	3	13	29	26	7	169	19	..	48
Serine	7	6	17	6	40	40	14	40	36	30	35
Leucine	1	13	..	11	27	29	44	6	32	18	75
Alanine	1	6	..	15	..	..	27	103	25	24	54
Valine	2	8	9	6	21	32	18	9	28	24	50
Glutamic acid	..	16	2	15	12	2	41	4	35	38	20
Threonine	..	2	11	7	28	35	16	4	16	16	24
Lysine	..	2	11	18	2	20	29	1	20	8	38
Arginine	40	2	5	2	2	6	6	2	15	48	14
Aspartic acid	..	5	5	6	25	11	18	6	16	14	33
Asparagine	..	8	11	4	16	20	14	..	16	31	18
Glutamine	..	4	11	4	16	20	14	..	17	32	18
Isoleucine	..	2	4	11	28	16	17	..	25	29	..
Proline	4	2	5	5	15	19	17	2	14	18	22
Phenylalamine	..	6	3	5	13	8	9	3	21	16	30
Tyrosine	..	8	7	2	16	6	8	19	9	12	11
Histidine	..	4	4	9	2	3	4	1	7	9	36
Methionine	..	..	5	2	4	3	8	..	16	8	4
Tryptophane	..	..	..	2	4	10	3	..	3	3	5
Cystine	..	6	4	..	2	5	3	..	1	2	1
Cysteine	..	..	1	..	2	4	4	..	5	2	3
Total amino acids	58	107	118	143	304	315	321	369	376	382	539

For numbers up to 100, a table of factorials may be found in "Handbook of Chemistry and Physics" (Chemical Rubber Publishing Co.), and use of that table will allow one to evaluate formula 2, readily enough, as 1.98×10^{24}. To make similar calculations for the other proteins in Table 1, values for various factorials of numbers greater than 100 are necessary. In such cases, use is made of Stirling's approximation formula:

$$n! \simeq \sqrt{2n\,\pi}\,(n/e)^n \qquad (3)$$

which can be simplified to:

$$n! \simeq \text{antilog}\,((n + 1/2)\log n - 0.4343n + 0.3991) \qquad (4)$$

By these methods, Table 2 can be prepared. Leaving the atypically simple protein, salmine, to one side, the number of permutations possible in the various proteins are tremendously higher than even Leathes' number.

A number of the order of 10^{619} (the largest in Table 2) is so vast that it and numbers like it are usually disposed of gingerly with the statement that it is too large for the human mind to comprehend. So it is, yet it could be amusing and even instructive, perhaps, to attempt to approach such a number in various ways.

For instance, is 10^{619} larger than the number of hemoglobin molecules on earth? To estimate whether this is so or not, let us take the human population of the earth as 2.5×10^9. If we assume that the average weight of a human being (including men, women, and children of all ages) is 55 kilograms, then the total weight of the earth's humanity is 1.4×10^{14} grams. Seven per cent of this quantity is blood and, taking the density of blood to be 1.06, there are 9.0×10^{12} ml. of human blood on earth. Since there are five billion red cells to the milliliter of blood, the total number of human erythrocytes on earth is 4.5×10^{22}.

The average volume of a human red cell is 90 cubic microns whereas the volume of a hemoglobin molecule (taking its measurements as $6.4 \times 4.8 \times 3.6$ millimicrons) is 1.1×10^{-7} cubic microns. Since one-third of the red blood cell is hemoglobin, we can see that each cell has room for 2.7×10^8 hemoglobin molecules. There are thus a total of 10^{31} human hemoglobin molecules on earth. If we make the generous assumption that the total amount of non-human hemoglobin on earth is a billion times that in the human species alone, the figure for hemoglobin molecules of all sorts is 10^{40}.

Nor are we through even yet. The average life of a human red cell is about a third of a year. Let us suppose that this is true for all species and that every time a new red cell is formed a completely new complement of hemoglobin molecules must be synthesized. The number of hemoglobin molecules existing on earth in a single year would therefore be 3×10^{40}. Even if we were to suppose that the total mass of hemoglobin on earth has been constant for the planet's whole range of existence of over three billion years (which is certainly overgenerous), then the total number of hemoglobin molecules that have ever existed on earth would be 10^{50}.

It is obvious, then, that 10^{619} is unimaginably greater than the total number of hemoglobin molecules that now exist or ever have existed. We can go further. It is far greater than the number of hemoglobin molecules that are likely to exist in the future. Consider that if every star in the universe (allowing the universe to contain a hundred million galaxies, each containing a hundred million stars) had three planets, each as rich in hemoglobin as the earth, and if the whole maintained a stable existence for a hundred billion years (quite too much to hope for cosmologically), the total number of hemoglobin molecules formed and destroyed in that interval would still be a mere 10^{68}.

Let us try another tack altogether. Suppose the existence of a cube, each edge of which is a billion light years long. Such a cube is large enough to contain, comfortably, the entire known universe from the earth to the farthest nebula. Imagine such a cube to be packed from end to end and top to bottom with hemoglobin molecules. The number it contained would be 10^{103}. If now every single second that entire vast array were replaced by a new set of molecules and this procedure were to continue for three hundred billion years, the number of hemoglobin molecules that would in all this time have existed would be just a little short of 10^{123}.

Let us be more generous still. Let us replace the hemoglobin molecule with that far tinier object, the individual neutron. Let us pack our cosmic cube with neutrons (with diameters of the order of 10^{-13} centimeters or 10^{-6} millimicrons) and replace them all every *fifth* of a second for three hundred billion years. The total number of neutrons would be 10^{144}.

And this number, too, which we have obtained by such stretchings of imagination, is only 10^{-475} of the number we are seeking to express. It is far less in comparison than is an electron to the universe.

Having considered all this, let us remember that a protein molecule is not merely a polypeptide chain, but may be several such chains coiled and bound together in an intricate three-dimensional lacework by a variety of subsidiary linkages, so that the possibilities of variations are far, far greater than those involving merely the order of the amino acids in a chain. Re-

TABLE 2
Amino Acid Permutation Possibilities in Various Proteins

Protein	*Number of possible permutations*
Salmine	1.98×10^{24}
Insulin	7.91×10^{113}
Ribonuclease	2.27×10^{126}
Horse myoglobin	6.44×10^{156}
Silk fibroin	2.54×10^{239}
Pepsin	1.10×10^{320}
Chymotrypsin	5.86×10^{355}
β-Lactoglobulin	4.08×10^{371}
Edestin	1.67×10^{445}
Ovalbumin	6.55×10^{461}
Horse hemoglobin	3.96×10^{619}

member, too, that hemoglobin is a protein of only average size and that giant proteins, such as those of which the genes consist, may be a thousand or more times as large.

It seems safe to conclude, then, that if anything in our finite, material universe can be said to approach the infinite, it is the versatility of the protein molecule and through that the versatility of life itself.

ASSEMBLIES FOR SUCTION FILTRATION

IRVING ALLAN KAYE and WILLIAM J. BURLANT
Brooklyn College, Brooklyn, New York

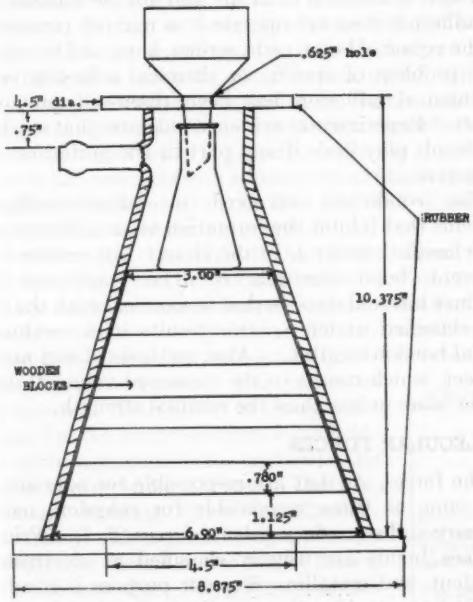


Figure 1. Filtration Assembly

THE filter bell shown in Figure 1, cut from a standard four-liter filter flask, has been used successfully for the past few years for collecting filtrates in Erlenmeyer flasks ranging in size from 50 to 1000 ml. The ground glass plate, an expensive feature in the apparatus described by Fieser,[1] has been replaced by a rubber mat. The 4.5-in. hole in the latter serves to secure the entire assembly to the laboratory bench when suction is applied. When cut from a two-liter suction flask, the

[1] FIESER, L. F., "Experiments in Organic Chemistry," D. C. Heath and Co., New York, 1941, p. 322.

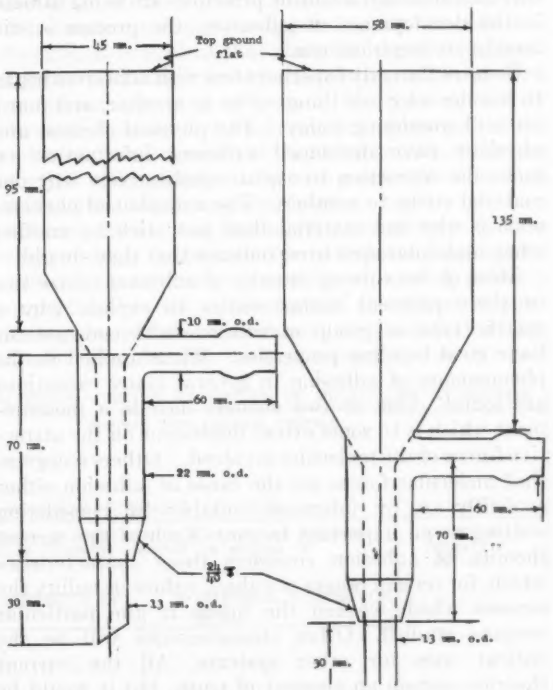


Figure 2. Filter Adapters

largest Erlenmeyer flask which can be accommodated is the 500-ml. size.

For filtering into standard taper vessels which can withstand strong pressure differentials (as ordinary round-bottomed flasks), the filter adapters illustrated in Figure 2 are more useful. The larger adapter has been used only with very large Büchner funnels.

NATURE OF ADHESION

FRANK W. REINHART
National Bureau of Standards, Washington, D. C.

THAT early member of the human race who accidentally found two pieces of material fastened strongly together with some fish residues or clay was probably astounded and curious. Later he or one of his brethren realized that this new principle could be used to advantage in the construction of some device, and as a consequence man became interested in adhesives from a practical standpoint. Someone along the line became dissatisfied with the products available and started varying the fish stews or mud pies to get a better adhesive. This experimentation was crude and empirical but improved adhesives were eventually developed. This process of improvement is still under way and although scientific principles are being utilized in the development of adhesives, the process is still largely an empirical one.

Some of the early experimenters with adhesives began to wonder why one thing sticks to another, and many are still wondering today. The physical chemist and physicist have developed sufficient information on molecular attraction to explain qualitatively why one material sticks to another. The unexplained phenomenon is why one material does not stick to another when molecular structures indicate that they should.

Most of the current theories of adhesion utilize two or three physical characteristics to explain why a specific type or group of adhesive-adherend systems have good bonding properties. When applied to the phenomenon of adhesion in general many exceptions are found. One or two authors include a measurement which is to some extent dependent on the attractive forces of the molecules involved. Others recognize that molecular forces are the cause of adhesion either explicitly or by inference, notably by considering wetting as an important factor. Each of the current theories of adhesion considers those characteristics which, for certain ranges of values, reduce or nullify the stresses which weaken the bonds in the particular systems studied. Other characteristics will be the critical ones for other systems. All the current theories contain an element of truth, but it would be advantageous to combine them all into an organized scheme which explains the source of adhesion forces and the effects of other characteristics of the system and conditions on the actual bond strength obtained.

It is intended to present a general outline of a theory of adhesion which will show in adhesive-adherend systems the qualitative relations among the causes of adhesion, the processes in bonding which allow these forces to become operative, the properties of the materials, and the changes in conditions which induce stresses. Individual factors involved in any specific adhesive-adherend system can be properly categorized and their effect on the bond strength evaluated on the basis of this outline. Some of the ideas set forth by various authors will be reviewed and placed in proper perspective in the general outline.

GENERAL THEORY

A general outline of a theory of adhesion is shown in graphic form in the chart. The cause of adhesion, *A* in the chart, is attributed to the molecular forces between the adhesive and adherend. Thus, it is assumed that adhesion is chemical in nature and not mechanical, that is, adhesion does not operate in a manner comparable to the action of bolts, nails, screws, keys, and interlocks. The problem of specific or chemical adhesion versus mechanical adhesion has been discussed previously (*1*, *2*). Experimental evidence indicates that mechanical bonds play little if any part in the performance of adhesives.

The conditions involved in adhesive-adherend systems that inhibit the formation of an adhesive bond are classified under *L* in the chart; this results in an inherent bond strength *B*. The conditions that produce internal stresses that weaken or break the bond are classified under *S;* this results in a residual or useful bond strength *C*. Also, methods of test are not perfect, which results in the measured value, *D*, being either more or less than the residual strength.

MOLECULAR FORCES

The forces, *A*, that are responsible for adhesion are the same as those responsible for cohesion, namely primary and secondary valence forces (*3*, *4*). Primary valence bonds are usually classified as electrostatic, covalent, and metallic. For our purpose it is advantageous to consider the coordinate-covalent bond as a fourth class, although it is recognized that it is a type of covalent bond.

Electrostatic or heteropolar (often simply called polar) bonds are those that hold atoms together in common salts. Compounds with bonds of this character ionize in solution. Electrostatic bonds are very seldom operative in adhesive bond formation. The strong bond between copper and sulfur in rubber compounds has been attributed to primary bond formation. Vinyl chloride resins containing maleic acid groups have been reported to bond to metals by the formation of an organic salt. However, since the

polarity or molar cohesion of the compound is increased by the introduction of this group, an increase in the secondary bonding forces also results (*5*).

Covalent bonds are those which hold atoms together in diatomic gases and in organic compounds. Two atoms share electrons so that each is stabilized. Bonds of the usual covalent type are more common in adhesive bonds formed between mineral products and metals than with organic materials. The bond formed when a silicone coating is applied to glass, by treating the glass with a chlorosilane, is of the covalent type (*6*).

The coordinate-covalent bonds are probably more common in adhesive bond formations in which an organic material is involved than either the covalent or electrostatic types. The ease of strong bond formation with materials containing carbonyl and hydroxyl groups is attributed to the formation of hydrogen bridges, a type of coordinate-covalent bond. The strong bonds formed between cellulose and many other organic materials are an outstanding example.

Metallic bonds are the type holding metals together and involve free electrons moving between the atoms in a continuous set of energy levels. Because of this state of electron fluidity, a metal has forces induced at its surface which are equal and opposite in charge to the force field of a material close to the metal surface. These two forces being opposite in charge create a strong bond provided the two materials are sufficiently near to one another. If polarity were the dominant factor in adhesion, then an adhesive would have as great an affinity for a metal or another material of similar polarity as it has cohesive strength.

Secondary or van der Waals forces arise from residual energies and are regarded as being weaker than primary valence bonds although in some cases they are of nearly primary magnitude. These forces are of greater magnitude for compounds than for atoms and molecules of elements. This indicates that unequal distribution of charges accounts for the larger residual force field. The more asymmetric the molecule, the greater the secondary forces. The predominant bonding forces in adhesion, particularly with organic compounds, are attributed to these van der Waals forces, which fall into three categories: orientation, induction, and dispersion.

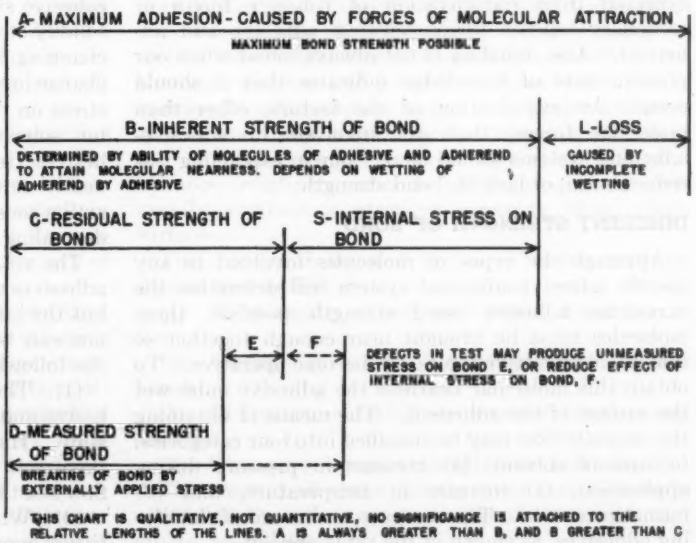
Orientation forces arise from the interaction of molecules in which the centers of mass of the positive and negative charges are not coincident because of asymmetric internal structure. These molecules possess a permanent electric moment or dipole. Organic molecules containing oxygen, nitrogen, sulfur, and halogens are of this type. Dipole molecules have attractive forces for one another and also exert an orienting influence on other molecules.

Induction forces arise from the interaction of molecules that have induced dipoles. These molecules have no dipole moment except under the influence of an electric field or molecules with permanent dipoles. These induced forces are smaller than orientation or dispersion forces.

Dispersion forces arise from the interaction occurring between electron systems because of constantly shifting electron positions. They are present in all molecules. These forces contribute greatly to cohesive strength. It is estimated that about 80 per cent of the total cohesion forces in most organic compounds arise from dispersion forces (*4*). The energy of these forces decreases by the sixth power of the distance between molecules and consequently the attraction is operative over only a very short range.

A study of the literature indicates that efforts to calculate the forces of cohesion, expressed as strength of materials, from measurements of the molecular forces of attraction, have been peculiarly unsuccessful. The values obtained in such considerations are many times the measured strength values. Since our present knowledge of the forces of molecular attraction is not sufficient to predict even approximately the cohesive strength, it is evident that the more complex problem of adhesive strength is far from solution in terms of the forces known to cause adhesion. Much more work by physical chemists and mathematical physicists on the nature and measurement of the forces holding molecules together will be needed to obtain more than the rough qualitative picture now available.

Frisch, Eirich, and Simha (*7*) showed recently that when a single large molecule is deposited on a solid surface from solution, the number of bonding points is proportional to the square root of the degree of polymerization. With contaminated surfaces and a large number of molecules, the proportionality factor would


A-MAXIMUM ADHESION-CAUSED BY FORCES OF MOLECULAR ATTRACTION
MAXIMUM BOND STRENGTH POSSIBLE
B-INHERENT STRENGTH OF BOND
DETERMINED BY ABILITY OF MOLECULES OF ADHESIVE AND ADHEREND TO ATTAIN MOLECULAR NEARNESS. DEPENDS ON WETTING OF ADHEREND BY ADHESIVE
L-LOSS
CAUSED BY INCOMPLETE WETTING
C-RESIDUAL STRENGTH OF BOND
S-INTERNAL STRESS ON BOND
E
F
DEFECTS IN TEST MAY PRODUCE UNMEASURED STRESS ON BOND E, OR REDUCE EFFECT OF INTERNAL STRESS ON BOND, F.
D-MEASURED STRENGTH OF BOND
BREAKING OF BOND BY EXTERNALLY APPLIED STRESS
THIS CHART IS QUALITATIVE, NOT QUANTITATIVE, NO SIGNIFICANCE IS ATTACHED TO THE RELATIVE LENGTHS OF THE LINES. A IS ALWAYS GREATER THAN B, AND B GREATER THAN C

be expected to be much less than one for the average of all molecules deposited.

Atoms or molecules on the surface of a solid will not have the same field of force as those in the interior. Those in the interior are surrounded on all sides by other atoms or molecules, whereas those on the surface have one free side. This free face offers an attractive force for other materials. Such a surface might be expected to bond readily to most molecules or atoms that could flow close enough to allow the molecular forces to become operative. If this surface is formed in air, it becomes contaminated immediately with layers of gaseous molecules such as oxygen and water. The first few molecular layers of gas are held by forces of the magnitude of the cohesive forces in the body of the material. A layer of gaseous or liquid material would not become very thick because of the low cohesive force holding these materials together.

Since the nature of the surface, whether contaminated or not, is different as regards molecular attractive forces from the body of the solid, it appears that measurements of bulk properties that are dependent on the force fields of individual molecules in the whole mass, such as dielectric constant and dipole moment, would not give any more than a qualitative expression for the maximum adhesive force. However, once another solid becomes bonded to this surface continuously over the whole interface, the surface forces would be partially satisfied. Consequently, measurements of the bulk attractive forces may in some cases come nearer to being useful for expressing the force of adhesion than is first apparent. Because of the many other factors involved, attempts to relate these measurements of molecular forces to measurements of adhesive bond strengths have been only partially successful (*8*, *9*, *10*, *11*).

The strength of most adhesive bonds, as they are measured and found in practice, is less than that expected from consideration of cohesive forces or secondary valence forces between adhesive and adherend. Also, bonding is not always found when our present state of knowledge indicates that it should occur. An examination of the factors, other than molecular forces, that are involved in adhesive-adherend systems should be of value in explaining this reduction in, or lack of, bond strength.

INHERENT STRENGTH OF BOND

Although the types of molecules involved in any specific adhesive-adherend system will determine the maximum adhesive bond strength possible, these molecules must be brought near enough together so that their attractive forces can become operative. To obtain this molecular nearness the adhesive must wet the surface of the adherend. The means of obtaining the requisite flow may be classified into four categories: (*a*) use of solvent, (*b*) increase in pressure during application, (*c*) increase in temperature, and (*d*) formation *in situ*. This serves as one means of classifying adhesives, as shown in the table opposite.

It is not sufficient for the adhesive to flow, since contaminants can change the character of the adherend surface to one which will have little or no attractive force for the adhesive being used. Also, bonding of the adhesive to a surface layer that is not strongly bonded to the body of the adherend will result in a weak structure although a strong adhesive bond is obtained. The principal reason for the washing, pickling, scouring, sanding, brushing, etc., of the surface of the adherend, stressed so much in directions for bonding operations issued by manufacturers of adhesives, is to produce a clean, sound surface.

In spite of all the cleaning operations, it is improbable in most bonding operations that an uncontaminated surface is obtained. The removal of all the water, atmospheric gases, and cleaning solvents is very unlikely. This means that the adhesive must displace or absorb the layer of surface contaminants on the adherend to obtain sufficient nearness for the molecular forces to become operative. The success of adhesives based on epoxy resins is attributed to their ability to displace or absorb the layer of adsorbed compounds on the surface of solid materials of many types.

Practical experience from working with adhesives, particularly the examination of broken adhesive joints, indicates that complete bonding of the area of the joint is not always obtained, even though the most careful precautions are taken to clean the surfaces prior to bonding. The strength of the bond, calculated in force per unit area, is necessarily reduced in these cases. This often accounts for the variability observed both in making strength tests and in the assembly of production parts.

INTERNAL STRESS

The adhesive must go through a fluid state to obtain molecular nearness for the bond to form, but, since liquid layers more than a few molecules thick have low cohesive strengths, it is necessary for the adhesive to solidify to obtain a strong joint. This process of changing from a liquid to a solid state results in a change in volume, usually a reduction, thereby creating stress on the bond. The changes in volume are great for solvent-sensitive and temperature-sensitive adhesives (see the table). The changes in volume are nearly zero for pressure-sensitive adhesives. For reaction-sensitive adhesives, the changes in volume vary depending on the particular chemical reaction involved.

The volatilization of solvents from solvent-sensitive adhesives usually causes a very large change in volume, but the internal stress on the bond from this phenomenon can be reduced appreciably by one or more of the following techniques:

(1) The most common technique is to use an adhesive material which is somewhat flexible in the dried state. Hard brittle materials are plasticized to render them soft and flexible. These soft materials tend to flow and thus relieve the internal stresses formed.

(2) When the surfaces of the adherends are relatively smooth and plane, the shrinkage is more likely to be uniform and draw the surfaces closer together.

Rough surfaces are more likely to cause voids, cracks, and nonuniform shrinkage, resulting in points for stress concentrations to develop.

(3) The layer of adhesive can be made thick enough so that the surface irregularities of the adherends are insignificant by comparison and the adhesive will flow sufficiently to relieve the stresses. Thin films of adhesive do not flow readily. However, relatively thick layers give weaker bonds. This indicates that for each adhesive-adherend system there is an optimum adhesive film thickness.

(4) The rate of volatilization of the solvent should be such that as the fluidity of the adhesive is reduced, the nearly-hardened adhesive will have sufficient time to flow and relieve the stresses being created.

(5) The most concentrated solution that it is possible to apply successfully should be used. An alternative to this technique is to apply the solution to the surfaces of the adherends, allow the adhesive to partially dry, and then bring the coated surfaces together.

Classification of Adhesives According to Method of Change from Liquid to Solid or Pseudo-solid State

	Class of adhesive	*Method of change from liquid to solid*
I.	Solvent-sensitive	Evaporation of solvent
II.	Pressure-sensitive	Release of pressure
III.	Temperature-sensitive	Decrease in temperature
IV.	Reaction-sensitive	Chemical reaction activated by catalysts, or heat, or both

The ratio of the coefficients of thermal expansion of the adherend and the adhesive is the controlling factor in the application of temperature-sensitive adhesives. Obviously, the nearer this ratio is to one, the lower will be the stresses produced by temperature changes. The magnitude of these stresses can be reduced by (*a*) using a flexible adhesive which will flow, (*b*) using adherend surfaces which are relatively smooth and plane, (*c*) using adhesive layers of optimum thickness, and (*d*) lowering the temperature slowly.

The types of material used in pressure-sensitive adhesives are soft, tacky, and flow readily. The application of low pressure causes the adhesive to flow sufficiently close to the adherend surface to result in bond formation. Bonds of this type are weak because of the flow characteristics and low cohesive strength of the adhesive.

The changes in volume with reaction-sensitive adhesives present a varied picture. When the adhesive is formed *in situ* and solidifies at a high temperature, stresses are produced by the change in volume on cooling in the same manner as with temperature-sensitive adhesives. The adhesives formed *in situ* at room temperature generally have small changes in volume. The change in volume in the formation of reaction-sensitive adhesives is dependent on the difference between the volume of the reactants and the volume of the cured adhesive. Some of the stress will be relieved in time if the final product exhibits some plastic flow. The use of thin layers of adhesive is very beneficial with this type.

Internal stresses on a bond may develop some time after the bond is formed. The factors which cause these stresses are changes in composition, changes in chemical structure arising from degradation of the molecule, and changes in temperature. The changes in composition arise from loss or gain of water, solvents, and plasticizers, depending on the exposure conditions; these cause changes in volume, modulus, flow characteristics, and possibly fundamental bonding force.

Degradation of the adhesive or adherend results in changes in chemical structure. Degradation may be caused by inherent instability or exposure to degradative forces such as heat and ultraviolet radiant energy and may be accompanied by changes in fundamental bonding characteristics, volume, and orientation, particularly in surface and interfacial layers. In addition, gaseous and liquid degradation products may be given off in such a manner that the bond is impaired. The reactions involved in forming an adhesive *in situ* may continue at a very slow rate, eventually resulting in additional changes in volume, modulus, flow characteristics, and chemical structure.

Adhesive bonds are often subjected in service to temperatures differing from those at which they were formed. The failure of bonds on cooling to low temperatures is not uncommon. This source of bond stress can be reduced by selecting materials so that the differences in coefficients of thermal expansion are as small as possible, or by using a material which will flow to relieve the stress developed and by cooling slowly so that flow can occur.

Surfaces that have a very rough topography and are nonuniform usually do not form bonds of the highest strength because of concentration of any stresses that may be present at places where voids or sharp changes in curvature occur. The increase in bond strength resulting from roughening surfaces is due mainly to the thorough cleaning and possibly to some extent to the increase in surface area. Given an adhesive-adherend system that has a potentially high strength because of the molecular forces involved and clean adherend surfaces, relatively smooth adherend surfaces will usually produce a stronger assembly than rough surfaces.

The causes of internal stress on bonds may be summarized as follows:

(1) Solidification of adhesive during bond formation.

(2) Changes in composition of adhesive and adherend.

(3) Changes in chemical structure of adhesive and adherend.

(4) Changes in temperature after bond formation.

The amount of stress arising from these causes is controlled by certain properties of the materials and design as follows:

(1) Moduli of elasticity of adhesive and adherend.

(2) Plastic flow of adhesive and adherend.
(3) Ratio of coefficients of thermal expansion.
(4) Thickness of adhesive layer.
(5) Design of joint.
(6) Surface topography.

The residual strength of the bond, *C* in the chart, is the inherent strength reduced by the losses arising from the internal stresses on the bond.

The design of the test specimens and the technique of applying the load in measuring bond strengths of adhesive-adherend assemblies usually result in obtaining a measurement *D*, less than the residual bond strength *C*. However, in some instances the applied force might act in such a manner as to relieve part of the internal stress on the bond and thus give measured bond strengths that are greater than the residual bond strengths.

SUMMARY

Adhesion is attributed to the forces of attraction between atoms and molecules, namely, electrostatic, covalent, and metallic bonds, and secondary or van der Waals forces. Secondary forces are probably responsible for most cases of adhesion, although the others are also operative in certain specific systems. These forces of attraction are operative to the extent that molecular nearness between adhesive and adherend is attained. This requires that the adhesive become liquid at some point or that it be synthesized in contact with the adherend. Changes in volume which arise from changes from the liquid to the solid state, changes in temperature, changes in composition, or changes on aging result in the development of stresses. The magnitude of these stresses is dependent on the moduli of elasticity, the flow, the ratio of the coefficients of thermal expansion of the adhesive and adherend, and the topography of the adherend surface. The strength of any particular system is thus dependent on the nature of the adhesive and adherend, the surface characteristics, the physical properties of the components, and the design of the joint.

A diagram is given to show the interrelations among the various factors involved in adhesive bonds. The factors discussed by various authors who have written on the theory or nature of adhesion can be placed in proper perspective by means of the diagram given. Each idea advanced to date is concerned with those properties of most importance in the particular system studied. This may account for the lack of universal acceptance of any one author's theory of adhesion.

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FIVE MILLION DOLLARS TO SPEND

A Class Project in Industrial Chemistry

J. RAE SCHWENCK
Sacramento Junior College and Sacramento State College, Sacramento, California

"WE HAVE five million dollars that we wish to invest in the development of an industrial chemical venture in our community. The chemical engineer who presents the plan that is eventually adopted will receive a permanent five per cent interest in the corporation. The engineer also will be retained as a consultant to insure the successful development of the industry."

Faced by this statement released by a well-known financier, what would you recommend?

This approach to a project assignment was tried recently at Sacramento State College with very interesting results. With modifications, the same approach has proved applicable to classes at any level. It provides a basis for the kind of thinking that more college students in chemistry ought to cultivate. This is a commercial world, a competitive world, and a creative world. Our young people should be encouraged to think commercially, competitively, and creatively.

The first class to be offered the opportunity to compete for this hypothetical five-million-dollar project was an upper-division class in industrial chemistry. As background, each member of the class had completed between 20 and 35 semester-hours in chemistry. They had made numerous field trips to industrial plants in the Sacramento and the San Francisco Bay areas. In their class work they had studied or surveyed some eighty major chemical industries. In these surveys emphasis was placed not only on chemical operation and control but also on industrial economics, national production curves, chemical process, and plant design.

For the industrial-chemistry class the assignment was given four weeks in advance. On the date set for reports the "Board of Directors" of the proposed corporation assembled in the conference room. Serving on the Board were Sacramento State and Junior College faculty members. They were pretending to be hard-headed, successful business men.

Each student was given 15 minutes in which to present his plan to the Board. He was to endeavor to convince the board that the venture into the industrial chemical field which would offer the maximum opportunity for financial return and ultimate expansion in the Sacramento area was the one that he had selected. The students were informed that the favorable decision of the Board was worth working for. Was he not to receive a five per cent interest if his plan were the one adopted? A five per cent interest in a five-million-dollar corporation could, if successful, produce a lot of dividends. The boys figured that they could worry about their income taxes later!

Each "consulting chemist or engineer," whichever he claimed to be, was to tell why he had selected his particular industrial plan. He briefly explained why others that had been suggested were, in his opinion, not as promising. His "sales talk" to the Board was required to include a brief consideration of plant location. Why is the particular location most desirable? What are the raw-material requirements? How great do the production and sales volume need to be in order to show a profit on the capital investment? What are the sales outlets and what does the market analysis indicate with regard to present and possible future competition?

The written report, left with the Board for their examination and independent evaluation, was to be in the form of a technical engineering prospectus showing plant design, reactions involved, operation-personnel requirements, and other data deemed important.

The results of this project were very gratifying indeed. Surprisingly enough, no two students were in favor of the same venture. Although the projects recommended were diverse, there were only three distinct types of plans presented. These three types are worthy of specific mention, for they throw some light upon the personality and the thought processes of the students presenting them.

One was the "single shot project," placing complete confidence in a well-organized plant that would produce a single product for a single outlet. This type of report placed confidence in the ability of its advocate to secure and control the market. According to his colleagues, this man was a gambler.

Another type was the "shot gun project" in which the student recommended so diversified a field of products that, he believed, some of them were bound to "click." Herein was noted a desire for security. Unfortunately, on one of this type of project the five million dollars would hardly have been able to make a start.

Several students advocated "waste material projects." Many dreamers have had their vision on the tremendous tonnage of agricultural waste material that is discarded in California every year. Chemicals from rice hulls and chemicals, including alcohol, from cull fruits were two projects in this category.

Needless to say, the sales arguments were heated, the

competition keen, and the loyalty to an idea commendable. In a few cases the thoroughness demonstrated by the students in their investigation of details, even to checking real estate costs and transportation contracts, was gratifying.

The enterprises most enthusiastically presented by the students, and also most favorably considered by the Board, have been those recommending the utilization of agricultural waste material. Perhaps our location has influenced this response. Whatever the contributing factors may be, it is significant to note that the industrial-chemical venture now in first place is the one which outlines the extraction of alpha-cellulose from rice hulls. One of the proposed outlets for this alpha-cellulose is in the manufacture of cellulose plastics. This same project further recommends the small scale, at present, manufacture of furfural and related chemicals.

ACKNOWLEDGMENT

The author wishes to acknowledge the assistance and suggestions of Dr. Hal D. Draper of Sacramento State College that led to the preparation of this paper.

A DYNAMIC ILLUSTRATION OF ORGANIC REACTION MECHANISMS

GUIDO H. DAUB, D. DONALD EVANS, and NOEL C. SORRELL

The University of New Mexico, Albuquerque, New Mexico

THE usual static methods of illustrating the accepted mechanisms of organic reactions, although satisfactory, can be rendered more effective in the classroom if supplemented with a dynamic or animated picture of the reaction as it proceeds. Such a dynamic representation of organic reactions has been developed.

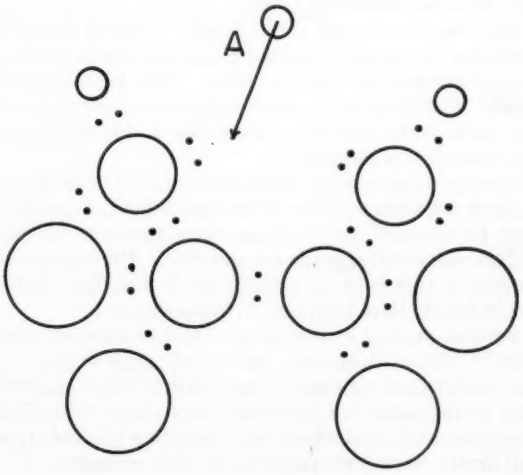


Figure 1

The method involves the use of a pack of 11 to 22 5 × 5-in. cards, more complex reactions requiring the larger number of cards. On each card is a picture of the molecule or molecules undergoing the specific reaction being illustrated. The positions of the atoms, electrons or groups on the successive cards are changed in such a manner that when one flips rapidly through the pack the reaction as well as its accepted mechanism is illustrated as a simple motion picture.

The construction of this visual aid is simple and inexpensive. The atoms or groups composing each molecule are represented by colored discs and electrons are represented by black dots, each dot representing one electron. The colors chosen to represent the various atoms are the same as those used in molecular model kits: black for carbon, orange for hydrogen, sky blue for nitrogen, indigo blue for oxygen, and green for chlorine. The methyl group is arbitrarily colored violet. The sizes of the atoms or groups are compatible with their respective atomic sizes and the actual diameters (in mm.) used are 10 for carbon, 4 for hydrogen, 9 for nitrogen, 9 for oxygen, and 13 for chlorine. The distance between atoms is arbitrarily chosen as 5 mm.

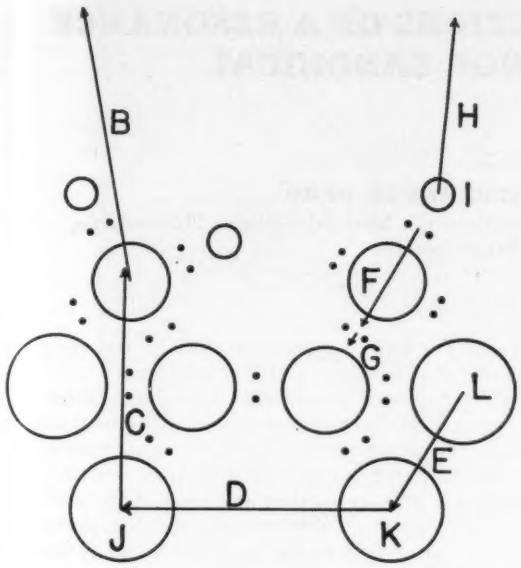
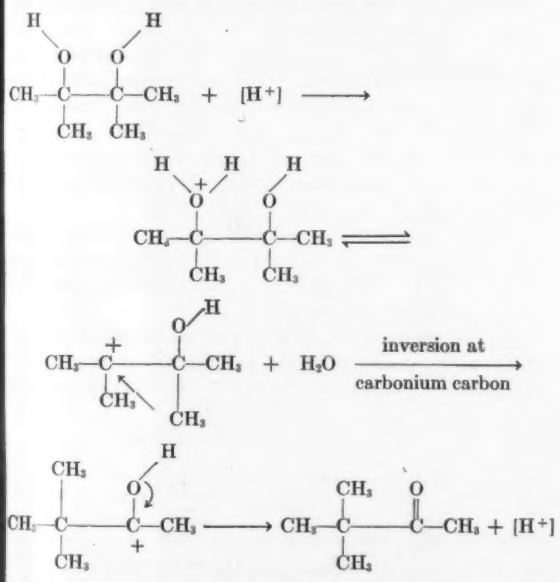
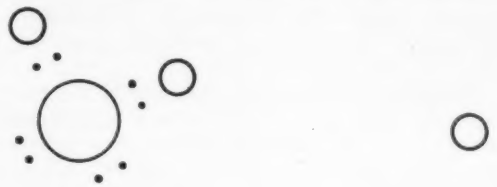


Figure 2

To illustrate the procedure used to prepare the cards for a single reaction, consider the pinacol rearrangement. The accepted mechanism for this reaction is illustrated below in the usual manner.



The construction of the dynamic illustration of this reaction is shown in Figures 1, 2, and 3. In Figure 1 is pictured a model of pinacol and the attacking proton (card 1) which initiates the reaction. The proton approaches the hydroxylic oxygen along path *A* in five increments requiring five additional cards. The structure thus obtained is shown in Figure 2. All of the shifts indicated in Figure 2 take place simultaneously in 15 increments on 15 cards. The molecule of water leaves by path *B*, methyl groups *J*, *K*, and *L* moving along paths *C*, *D*, and *E* respectively. Proton *I* leaves by path *H* with a simultaneous shift of electrons along *F* and *G* to form a carbon-to-oxygen double bond. The picture thus obtained on card 21 is shown in Figure 3 and represents the completed reaction. Flipping rapidly through the cards produces an active illustration of the pinacol rearrangement.



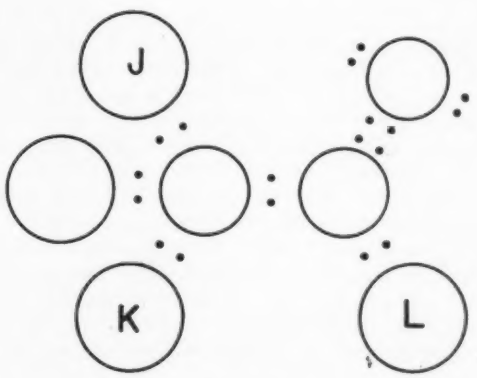


Figure 3

Other reactions whose mechanisms have been illustrated in this way are the S_{N2} displacement, S_{N2}' displacement, Demjanow rearrangement, Cannizzaro reaction, dienone-phenol rearrangement, Michael reaction, diazomethane ring enlargement, benzoin condensation, and benzilic acid rearrangement.

PREDICTING REACTIONS OF A RESONANCE HYBRID FROM MINOR CANONICAL STRUCTURES[1]

ALEXANDER GERO
Hahnemann Medical College, Philadelphia, Pennsylvania

IT IS customary to define resonance in chemistry as the phenomenon in which the behavior of a compound can only be described by a combination of several structural formulas (canonical structures) rather than by one structure alone. The properties of the compound are intermediate between those one would expect from each canonical structure.

Except for the statement that one of the canonical structures, that of the lowest energy content, contributes most to the properties of the resonance hybrid, little effort seems to have been made in textbooks (or, for that matter, in original papers) to set up any general rules on the contributions of the several structures to the reactions of the hybrid.

In the experience of this writer, such rules can be set up and used profitably to illuminate this difficult subject for students.

The basis of our approach is the same as for an understanding of resonance energy (*1*), namely, an emphasis on the energy levels and on the greater stability of a lower energy level. On this basis, it is easy to understand that the lowest-energy structure contributes most to the state of a resonance hybrid, *i. e.*, its *static* properties, such as bond lengths. By the same token, it may be expected that more can be learned from the higher-energy structures about the *dynamic* properties of the hybrid, *i. e.*, its reactions, for stability and reactivity are opposites, and higher energy level means lower stability, hence greater reactivity. In other words, we look to the principal canonical structure for the physics of a resonance hybrid, but to the minor structures for its chemistry.

We do this by arranging in order of decreasing stability all those canonical structures of a resonance hybrid which are not so improbable as to make no significant contribution. In setting up this arrangement, we follow such simple criteria as completeness or incompleteness of electron shells, presence or absence of charge separation, etc. Then we pick out the last, *i. e.*, least stable, structure in the list (we term it the "critical structure"), find that point in it which is most responsible for its instability (the "critical point"), and try to predict in what way it might tend to relieve its instability. This, we presume, will be the most likely course of the reactions of the compound.

This approach is somewhat reminiscent of the theory of molecular diagrams developed by Daudel and Pullman (*2*) which uses only the excited structures of aromatic molecules in predicting their reactions. Our approach is more modest and more conservative, but at the same time more general, and has proved most fruitful in predicting the reactions of many resonance hybrids. The rest of this paper will be devoted to examples of its application.

Addition Reactions of Carbonyl Compounds. Of the two resonance structures of the carbonyl group,

$$\underset{\text{(I)}}{R_2C{=}O} \longleftrightarrow \underset{\text{(II)}}{R_2C^{+}{-}O^{-}}$$

obviously (I) represents a lower energy level than (II) because charge separation in the latter represents energy input. Within this structure the carbon atom, with only a sextet of electrons, is the critical point which determines the reactions through its instability. Therefore we expect carbonyl compounds to be primarily electrophilic agents at the carbonyl carbon. This was indeed the result of Lapworth's classical investigations on acetaldehyde (*3*).

(The mobility of the α-hydrogen in carbonyl compounds is readily understood from a third contributing structure, $H^{+}\ CH_2{=}CH{-}O^{-}$, in which the lone proton is the critical point.)

Hydrolysis of Esters. The base-catalyzed hydrolysis of esters is closely related to the addition reactions of aldehydes. In esters structure (II) is the critical

$$\underset{\text{(I)}}{R{-}\overset{\overset{OR'}{|}}{C}{=}O} \longleftrightarrow \underset{\text{(II)}}{R{-}\overset{\overset{OR'}{|}}{C^{+}}{-}O^{-}} \longleftrightarrow \underset{\text{(III)}}{R{-}\overset{\overset{\overset{+}{O}R'}{\|}}{C}{-}O^{-}}$$

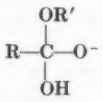
structure with its electron sextet, just as in aldehydes and ketones, and makes the ester molecule electrophilic or, in the Lewis terminology, acidic. It can therefore react with the base H_2O to form the nonresonating dipolar ion,

$$R{-}\overset{\overset{OR'}{|}}{\underset{\underset{\overset{+}{OH_2}}{|}}{C}}{-}O^{-} \rightarrow R{-}\overset{\overset{OR'}{|}}{\underset{\underset{OH}{|}}{C}}{-}OH$$

[1] Presented before the Division of Chemical Education at the 123rd Meeting of the American Chemical Society, Los Angeles, March, 1953.

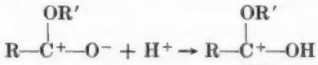
which, lacking resonance, will be unstable relative to a molecule stabilized by resonance such as RCOOH. Therefore it will lose R′OH and break down to a carboxylic acid.

Obviously, such a reaction, in which the ester functions as an acid, proceeds even more readily in the presence of a stronger base than H_2O, for instance, OH^-. In that case, instead of the nonresonating dipolar ion, a nonresonating anion is formed,



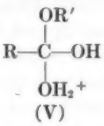
which breaks down analogously, this time to the more stable anion $RCOO^-$.

However, in a strongly acidic medium the electrophilic tendency of the carbonium ion is frustrated. But (II) is still the critical structure, and if the presence of a strong acid prevents it from reacting as an acid at its carbonium ion, it will react as a base at its negative oxygen:



(IV)

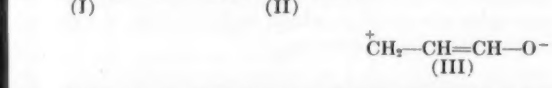
Now the cation (IV) is certainly a stronger acid than the dipolar ester molecule; hence it will react more readily with the base H_2O. The result is a nonresonating cation (V) which breaks down, as before, into ROH_2^+



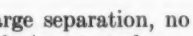
(V)

and the resonating molecule RCOOH.

Addition to α, β-Unsaturated Aldehydes and Ketones. Such compounds have three canonical structures:



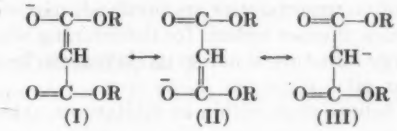
(I) (II)



(III)

of which (I) is most stable (no charge separation, no electron sextets) and (III) least stable (greatest charge separation). Consequently, (III) is the critical structure, and the carbonium ion in it, with its sextet, the critical point. At the same time, structure (II) also contributes to the reactivity of the hybrid, the critical point being in this case the carbonyl carbon. However, if electron-releasing groups are attached to the carbonyl group the electron deficiency of the carbonyl carbon is alleviated and the stability of structure (II) increased. This leaves structure (III) as the one most important high-energy structure for determining the reactions of the hybrid; hence α, β-unsaturated ketones show greater tendency toward 1,4-addition (*e. g.*, of Grignard compounds) than the corresponding aldehydes.

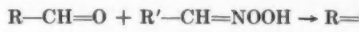
Malonic Ester Synthesis. Malonic ester anion, too, has three canonical structures:



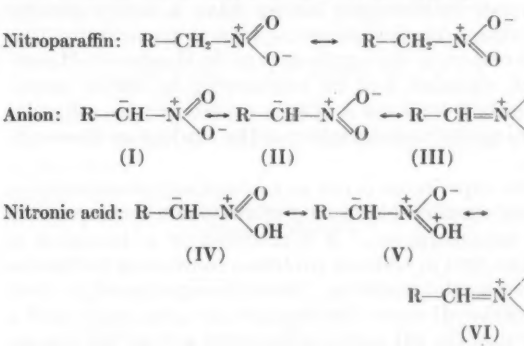
(I) (II) (III)

none of which shows instability in the form of either charge separation or an electron sextet. But since carbon, with its lower electronegativity, can hold unshared electron pairs less easily than oxygen, (III) must be the critical structure, and the carbanion in it the critical point. Hence reaction with carbonium ions must lead to C-alkyl derivatives, as experience shows.

The Condensation of Aldehydes with Nitroparaffins. This reaction is supposed to proceed by way of the nitronic acid isomer of the nitroparaffin since neither the nitroparaffin nor its anion reacts; reaction occurs only when weak acid is added to the anion (*4*):



As far as the aldehyde goes, this reaction conforms to the pattern discussed above. As to the nitroparaffin, it is instructive to consider the resonance of the true nitroparaffin, the anion, and the nitronic acid:



(I) (II) (III) (IV) (V) (VI)

We see that the nitroparaffin has two identical resonance structures; hence it is stable. The anion should also be stable, despite the carbanion in (I) and (II), because it has three canonical structures, of which two, (I) and (II), are identical. Of the three structures of the nitronic acid, however, no two are identical, and two of them, (IV) and (V), contain an unstable carbanion. (V) is the least stable structure because it has the most charge separation and two positive charges on neighboring carbon atoms. Therefore, (V) is the critical structure, and the carbanion in it the critical point which can serve as the nucleophilic agent required by the electrophilic aldehyde.

These few examples should suffice to show the applicability of our principle. It is, of course, not claimed that it is either radically new or 100 per cent foolproof. Several authors have spoken of this or that point in a molecule as being the "driving force" of a

reaction, but only in an offhand way. The writer and his students believe they are first to have used this approach systematically. They are aware of its limitations: too often uncertainties are involved, particularly in the absence of exact criteria for determining whether a high-energy structure is not so unlikely as to be of no influence at all.

Still, we believe that, within its limitations, attention to minor canonical structures in predicting reactions is a method of proven didactic value.

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VERIFICATION OF THE HENDERSON-HASSELBALCH EQUATION

R. QUENTIN BLACKWELL and LEONARD S. FOSDICK
Northwestern University Dental School, Chicago, Illinois

THE accurate conception of buffers and buffer action is extremely important in a number of phases of biochemistry. We have found that many students coming into our biochemistry classes have a rather sketchy knowledge of the subject. This is particularly true with respect to the significance of the Henderson-Hasselbalch equation and its relationship to buffer action. Accordingly we use a simple experiment to aid in increasing the understanding of the student on these subjects.

The experiment is run as a laboratory demonstration with a considerable amount of discussion accompanying the demonstration; it is preceded by a discussion of buffers, and in addition problems concerning buffers are solved by the students. Since the experiment involves use of the pH meter the schedules are arranged in such a way that the pH meter is discussed and its use demonstrated in the laboratory period preceding the one in which the buffer experiment is presented.

The experiment itself is simply a comparison of the actual pH of buffer solutions with the theoretical pH as predicted by the Henderson-Hasselbalch equation. For simplicity 0.1 *M* solutions of acetic acid and sodium acetate are used, and the pH's of various mixtures of the two solutions are measured. The data obtained in the demonstration are recorded by the students in a table supplied in their mimeographed laboratory manual. A reproduction of the table appears below. The necessary calculations are made by the students to fill in the empty columns in the table; when the table is filled it provides a comparison of calculated and observed pH values for the various mixtures of salt and acid. The agreement is usually within approximately 0.1 pH unit, which illustrates the validity of the equation.

Following the demonstration a short discussion emphasizes the mechanism of buffer action, and numerous examples are cited in which buffer action is extremely important in biochemistry.

Solution	*Vol. of 0.1 M acetate*	*Vol. of 0.1 M acetic acid*	*Conc. of acetate [salt]*	*Conc. of acetic acid [acid]*	$\frac{[Salt]}{[Acid]}$	$log \frac{[Salt]}{[Acid]}$	*Calculated pH*	*Observed pH*
1	10.00	0.00			∞	....	....	
2	9.90	0.10						
3	9.50	0.50						
4	9.00	1.00						
5	8.50	1.50						
6	8.00	2.00						
7	7.00	3.00						
8	6.00	4.00						
9	5.00	5.00						
10	4.00	6.00						
11	3.00	7.00						
12	2.00	8.00						
13	1.50	8.50						
14	1.00	9.00						
15	0.50	9.50						
16	0.10	9.90						
17	0.00	10.00			0	....	....	

DETERMINATION OF THE DENSITY OF OXYGEN GAS

B. A. FIEKERS, S. J.
College of the Holy Cross, Worcester, Massachusetts

A VERY convenient source of oxygen is provided by the "Oxybomb."[1] It is a small, $2^1/_2$ by $^5/_8$-inch cartridge of compressed oxygen that resembles a carbon dioxide source, such as the "Sparklet," for carbonating water in a siphon bottle. The cartridge of oxygen comes fitted with a threaded collar so that a specially designed needle valve can be attached to it for puncturing the soft metal gas seal and for controlling the flow of gas. It is the purpose of this paper to show how this oxygen source can be used for determining the density of oxygen gas in laboratory or lecture.

All currently popular laboratory manuals describe the chemical generation of oxygen, one of them recommending the thermal decomposition of lead peroxide (*1*); all of the others, such as Holmes (*2*), the thermal and catalytic decomposition of potassium chlorate. Possibly the method proposed in this paper has a pedagogical advantage in separating the physical aspects of the gas laws from the chemical preparation of the gas. It would give the student fewer principles to learn in a unit exercise and this might appeal to some instructors. Further, this exercise consumes but little time. It may thus be of value to instructors who are seeking alternative exercises to fit given time schedules. At any rate, this experiment can be used for demonstration to groups in the laboratory alongside the traditional counterparts which give equal emphasis to the chemical and the physical principles involved.

PROCEDURE

The following procedure is recommended for student exercises in determining the density of oxygen and checking the molecular weight of a given sample.

Set up a one-liter gas bottle in a pneumatic trough. Fill the bottle with water in the usual way and avoid the presence of air bubbles in the bottle. Provide a gas inlet with a suitable length of rubber tubing which will fit the needle valve snugly and yet allow for ready connection and disconnection. Attach the needle valve tightly to the cartridge of gas, taking care not to puncture the gas seal. Weigh the cartridge and valve, without the rubber tubing, on a triple beam balance and estimate the weight to the third decimal place in grams. Then connect the rubber tubing to the valve.

In order to puncture the seal, first turn the valve-head down loosely until contact between needle and seal is established. Then advance the screw successively about half a turn forward and a quarter turn backward until, at any backturn, gas bubbles into the bottle. As soon as the seal is known to be punctured cut down the flow of gas to about one bubble per second. Allow the gas to replace the water in the bottle until the same water level in the trough and bottle is reached. Then disconnect and weigh the cartridge again and get the weight of the released oxygen by the difference between this and the original weight of the cartridge (ΔW). Slip the mouth of the inverted bottle over a glass plate under water, maintaining equal water levels as far as possible. Then invert the bottle briskly so that it neither gains nor loses water (practice). Now measure the volume of oxygen in liters (V_l) by filling the gas bottle to the brim with water from a graduated cylinder. Take the temperature ($T_{abs.}$) of the water. Get the barometric pressure in millimeters of mercury, making instrumental corrections, and correct for the vapor pressure of water as well ($P_{cor.}$). Calculate the density (d) of oxygen gas at standard conditions.

$$d = (760 \times T_{abs.} \times \Delta W)/(273 \times P_{cor.} \times V_l)$$

Multiply the density by 22.4 and see if it checks the molecular weight of oxygen. Sample results are given in the table.

Sample Results

Detn.	*A*	*B*
ΔW(g.)	1.125	0.954
V(l.)	0.930	0.790
T(abs.)	301	301
P(cor.)	711	711
d(g./l.)	1.426	1.423
Mol. wt.	32.0	31.9

In this experiment if the needle is driven all the way in and then withdrawn from the gas seal, it cannot always be closed tightly again and gas is apt to leak during the second weighing. Further, if the gas is allowed to flow too rapidly into the bottle, the results may come out too high. It seems that pressure and consequent leakage in the head of the valve can be minimized by slowing down the flow of gas as directed. The valve is obviously not designed for quantitative applications.

Lecture or group demonstrations can be speeded up by weighing the cartridge beforehand; by releasing the oxygen to a predetermined volume so that the corresponding cartridge weight can be anticipated by calculation; and then by weighing the cartridge with the weights thus set beforehand. It is essential only to

[1] The "Oxybomb" and needle valve are marketed by A. Daigger & Co., 159 West Kinzie St., Chicago 11, Ill.

show that a balance is struck before the weight data are taken.

According to most laboratory manuals, such as Sisler and Stewart (*3*), the chemically generated gas is passed into a filled wash bottle in such wise that the displaced water is ejected. The volume of the gas is taken as the volume of the ejected water. A cartridge source of gas can also be used with this technique.

According to a few laboratory manuals (*1*, *4*), on the other hand, the traditional method of using the pneumatic trough is employed. In such instances, the amount of chemical used has to be planned carefully so that the volume of gas will not exceed the capacity of the container. Further, both the oxygen source and the catalyst have to be dried.

Oxygen is the gas chosen in all laboratory manuals that list the experiment. The procedure here suggested may eventually make possible a choice of diverse gases.

The experimental objective given by most of the laboratory manuals is the determination of the density of the gas. One (*1*) laboratory manual chooses to evaluate the gas constant *R;* another (*5*) evaluates the molecular weight of oxygen.

Other gases are commercially available in cartridge form: among them, carbon dioxide, as already mentioned; nitrous oxide for whipping cream; and isobutane, recently introduced for cigarette lighters. Because of their solubility in water, they are not suitable materials for this experiment. One would need the services of a good mechanic to construct safe valves for these before they could be pressed into general laboratory service. It is hoped that a large number of common laboratory gases will be made available in some such form.

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WALTER HIEBER

RALPH E. OESPER
University of Cincinnati, Cincinnati, Ohio

AT ITS general meeting in Cologne in 1951, the Gesellschaft Deutscher Chemiker awarded its Alfred Stock Memorial Prize. The citation read: "To Professor Dr. rer. nat. Walter Hieber, director of the inorganic chemical laboratory of the Technical University in Munich, eminent investigator in the field of complex compounds, who with masterful command of the preparative methods and deep understanding of the theoretical problems has developed the domain of the carbonyl and nitrosyl compounds and obtained results valuable both to pure science and technology."

Walter Otto Hieber was born at Stuttgart, capital of Württemberg, on December 18, 1895.[1] Four years at the University of Tübingen (1914-18) culminated in the doctorate. The dissertation was prepared under the guidance of Rudolf Weinland (1865–1936).[2] At the University of Würzburg, where he was assistant to Otto Dimroth (1872–1940),[3] Dr. Hieber habilitated as Privatdozent in 1924. The next year he went to the University of Jena as associate professor and head of the inorganic-analytical section and in 1926 he was called to the University of Heidelberg in the same capacity. In 1932 he accepted a teaching post at the Technical University of Stuttgart where he taught general, inorganic, and analytical chemistry and was advanced to the acting headship of this Institute, in 1933. In 1935 he was called to the Technical University of Munich as full professor of inorganic chemistry, general experimental chemistry, and analytical chemistry and

[1] His father, Johann von Hieber, Ph.D., J.D. (h.c.), Agr. D. (h.c.), served as Staatspräsident of this German state.

[2] For biographical details see HIEBER, W., *Ber.*, **69**, 210 (1936).
[3] For biographical details see EMMERT, B., *ibid.*, **73A**, 94 (1940); HARMS, F., *ibid.*, **74A**, 1 (1941).

director of the inorganic chemical laboratory. His predecessor in this important post was Wilhelm Manchot, who likewise had a reputation as a student of nitrosyl and carbonyl compounds.

Professor Hieber's researches deal mainly with complex compounds. Among the various categories he has investigated are: cyclic molecular compounds; the complex chemical behavior of oximes, aromatic diamines, and ethanolamines; heats of formation and the constitution of complex metal halide compounds; the complexes of bivalent silver and quadrivalent nickel.

Professor Hieber has been especially interested in the metal-carbon monoxide complexes, particularly the metal carbonyls, since 1927. He and his collaborators have published more than the 80 papers, including 60 experimental studies, in this field, which previously had been investigated to only a comparatively small extent from the standpoint of modern ideas. The study of the reactions and investigation of derivatives of the metal carbonyls, especially the amine- and alcohol-substituted carbonyls, led to the discovery of the "metal carbonyl hydrides" of iron (1931) and soon thereafter to those of cobalt. The elucidation of the "base reaction of iron pentacarbonyl" came in 1932. The nitrosyl-carbonyls of iron and cobalt were studied with the assistance of J. St. Anderson in 1932, and since 1940 Hieber and his school have greatly extended the field of nitric oxide complexes.

He has systematically studied the pressure synthesis of metal carbonyls (from 1939 on). Through new pressure syntheses of the carbon monoxide compounds of the metals of the iron and chromium groups, he has arrived at the discovery and preparation of new carbonyls and carbonyl halides of the noble metals, *i. e.*, rhodium, iridium, osmium, and particularly rhenium.

More recently (1950–52) substitution reactions with isonitriles have yielded nickel tetraisonitriles and isonitrile-substituted metal carbonyls. These reactions have led to a new conception of the formation-mechanism and the structure of the amine- and alcohol-bearing carbonyls. Methods of forming and producing carbonyls from nickel and cobalt salts under normal laboratory conditions have been worked out.

Walter Hieber

The metal carbonyl hydrides are now being characterized, on the basis of their acidic nature and physicochemical behavior, from the standpoint of the present-day ideas of structure and valence. As a whole, the chemistry of carbon monoxide, like that of the nitric oxide complexes, has contributed in special measure to the refinement and deepening of our valence concepts and to the growth of the theory of coordination chemistry.

Professor Hieber is a member of the Bavarian Academy of Sciences. His name appears on the masthead of the *Zeitschrift für anorganische und allgemeine Chemie*.

MERCURY CONTACT FOR CONSTANT TEMPERATURE THERMOREGULATOR[1]

MICHAEL CEFOLA and ARTHUR J. CHADWICK
Fordham University, New York City, New York

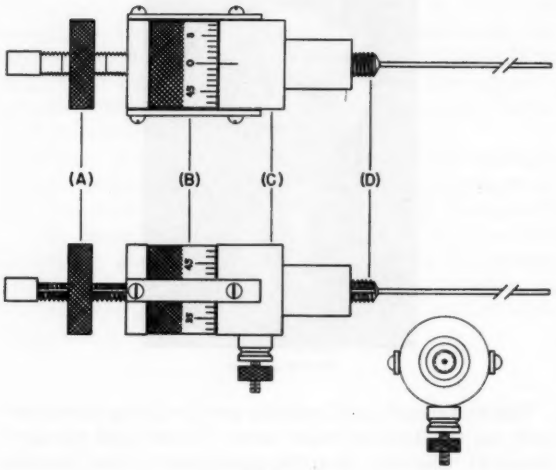

Figure 1

A DEVICE for the precise regulation of temperature in constant temperature baths has been constructed and used with very good results in our laboratory. This instrument, after calibration, eliminates the "hit or miss" control that is necessary with ordinary regulators.

The essential constructional features of the mercury contact herein described are illustrated in Figures 1 and 2. Regulation of the temperature is brought about by the rotation of the calibrated drum *B* (Figure 1) about the stationary member *C*. This causes the threaded spindle *D* to move up or down, as a result of which the needle-like steel wire at the end of the spindle will make or break contact with the mercury thread in the capillary of a glass thermoregulator. Stainless steel is to be preferred for part *D* because of its great resistance to corrosion. The drum *B* has 50 divisions and the number of threads on screw component *D* are such that one small division is equivalent to 0.001 inch. To facilitate keeping track of the distance of movement of the needle the flat portion of spindle *D* is marked in quarter inches, each equivalent to 250 units on the drum *B*. Part *A* is simply a "lock-nut" to prevent the movement of *B* once the setting has been chosen. Very specific details of the construction of the various component parts of the mercury contact are shown in Figure 2.

The device may be calibrated with the aid of a Beckman thermometer immersed in the bath and

[1] Based in part on work performed under contract for the Atomic Energy Commission, New York Office.

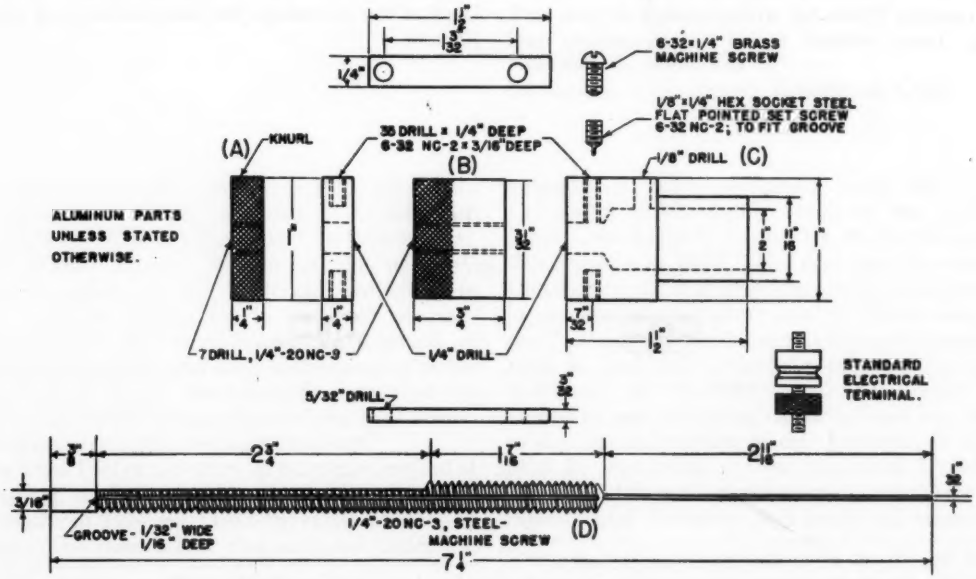
6-32×1/4" BRASS MACHINE SCREW
1/8"×1/4" HEX SOCKET STEEL FLAT POINTED SET SCREW 6-32 NC-2; TO FIT GROOVE
(A) KNURL
36 DRILL × 1/4" DEEP 6-32 NC-2 × 3/16" DEEP
(B)
1/8" DRILL (C)
ALUMINUM PARTS UNLESS STATED OTHERWISE.
7 DRILL, 1/4"-20 NC-3
1/4" DRILL
5/32" DRILL
STANDARD ELECTRICAL TERMINAL.
GROOVE - 1/32" WIDE 1/16" DEEP
1/4"-20 NC-3, STEEL-MACHINE SCREW
(D)

Figure 2

indicating the temperature obtained with each setting of the calibrated drum. Enough time is allowed after each adjustment of the setting to insure the attainment of constant temperature. The precision of the instrument was tested by starting at the lowest setting of the drum and then making frequent changes until the maximum temperature range was reached. This was followed by a repetition of the drum settings in such a way that the temperature was brought down on exactly the same course as it was taken up. The data obtained for the particular glass thermoregulator in use in our laboratory are shown in the table. The temperatures recorded are in degrees centigrade and the drum settings in inches.

By plotting average temperature values versus drum settings a calibration curve may be constructed, as shown in Figure 3, from which any desired temperature may be obtained for the bath by the appropriate choice of drum settings. With our instrument the precision of such calibration was better than 0.02°C. The range of working temperatures will of course depend upon the particular combination of capillary tubing in the thermoregulator and upon screw length.

Temperatures in °C. at Various Drum Settings

	Drum setting				
Exp. no.	1.250	1.000	0.750	0.500	0.250
1	25.720	26.839	28.024	29.205	30.393
2	25.660	26.842	28.037	29.236	
3	25.650	26.830	28.039	29.203	30.399
4	25.635	26.859	28.041	29.210	
5	25.683	26.880	28.015	29.194	30.397
6	25.663	26.827	28.006	29.210	
Av. temp.	25.668	26.846	28.027	29.210	30.396
Av. deviation	±0.022	±0.016	±0.012	±0.009	±0.002

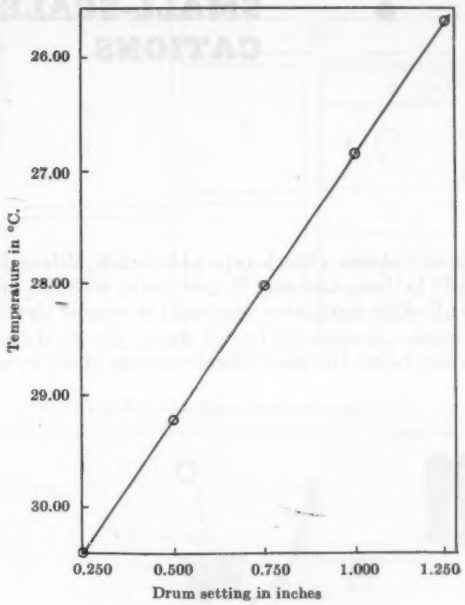

Figure 3

An immediate improvement in the apparatus consists in the tapering of the lower member of part *C* in Figure 1 so that it may fit a standard taper female joint attached to the upper end of the glass thermoregulator

TECHNICAL WRITERS' INSTITUTE

THE second annual Technical Writers' Institute will be held at Rensselaer Polytechnic Institute, Troy, New York, beginning Monday, June 21, and running through Friday, June 25.

As was last year's session, when 24 companies participated, the Writers' Institute is designed for those who supervise technical writing in business and industry, educational programs, and promotional work. It gives instruction and refresher work in all phases of technical writing.

Included in the course of study and discussions are sessions on operational manuals, reports, direct business communications, company-public relations, and associated fields. The week is devoted to group discussions, lectures by outstanding authorities, personal consultations, and writing practice exercises.

The Technical Writers' Institute is a service of the Rensselaer Extension Group.

SMALL-SCALE UNITS FOR ORGANIC IDENTIFICATIONS

JOHN T. STOCK and M. A. FILL
Norwood Technical College, London, England

FIGURE 1 shows a block-type unit which, although less than 11 in. long and only $3\frac{1}{2}$ in. wide, includes practically all of the apparatus required for organic identification work. To provide burner space, the wood block is cut away below the sheet aluminum top plate, in which

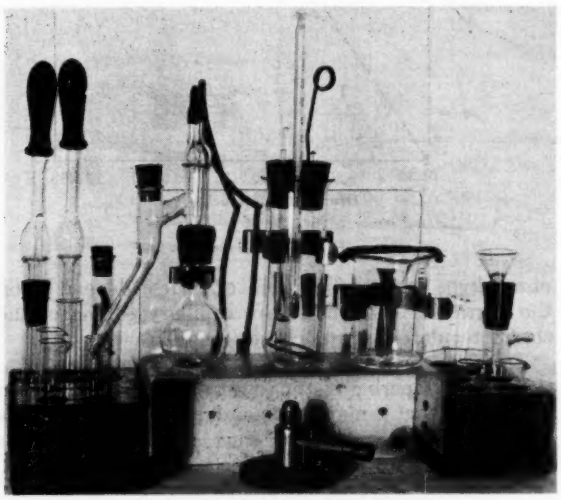

Figure 1. Unit for Organic Identifications

there are three $\frac{3}{4}$-in. holes. A $\frac{1}{8}$-in. vertical panel of transparent Lucite is screwed to the back of the burner space and is faced with $\frac{3}{16}$-in. asbestos sheet below the top plate to prevent distortion during heating operations. The panel carries "Terry clips," in which are mounted a 50-ml. beaker serving as a water bath, a melting-point apparatus, and a 20-ml. flask carrying a "reflux-or-distill" attachment.

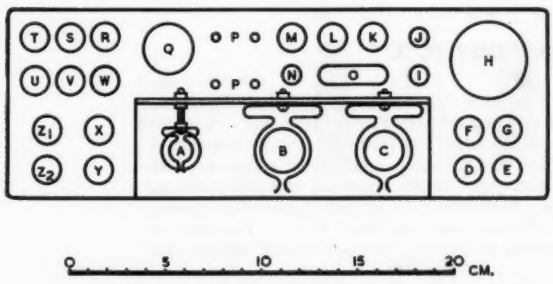

Figure 2. Location of Apparatus in Unit

A, "Reflux-or-distill" apparatus with flask; *B*, melting-point apparatus; *C*, water bath; *D*, *E*, crystallising tubes, small; *F*, glass rods; *G*, Willstätter "nail" filter and receiver; *H*, ice bath; *I*, sodium needle; *J*, tweezers; *K*, filter discs; *L*, bumping stones; *M*, small corks; *N*, melting-point tubes; *O*, microscope slides and ignition tubes; *PP*, water connections; *Q*, spare flask (stored inverted); *R*, litmus papers; *S*, *T*, teat pipets; *U*, microspatula; *V*, *W*, micro test tubes; *X*, *Y*, receivers; Z_1, Z_2, crystallizing tubes, large.

Holes bored in the top of the block as indicated in Figure 2 accommodate the various pieces of apparatus listed in the caption. The delivery arm of the distillation apparatus is arranged to swing across the mouths of receivers *X* and *Y*, thus allowing fractions to be collected when required. The general arrangement is such that the apparatus needed most frequently is toward the front of the block.

Heat is supplied by a Bunsen burner from which both flame-tube and base have been removed. Provision of a new base in the form of a cut-down 2-in. Bakelite reagent bottle cap, as shown at (*a*) in Figure 3, enables the microflame to be placed directly under any one of the holes in the top plate. The container of the melting-point apparatus is a 100 × 30-mm. heavy grade boiling tube. To permit insertion and withdrawal of melting-point tubes without dismantling the apparatus the cork carries an entry tube and a footlike support of glass rod, as shown at (*b*). A 6-in. thermometer, reading to 200°C. and available at about the same price as the commoner 12-in. version, is used for the sake of compactness. Removal of a narrow sector of cork in front of the thermometer scale renders the whole of the latter visible.

The "reflux-or-distill" attachment shown at (*c*) in Figure 3 is particularly useful for small-scale work. Stillhead *A* is held snugly in the mouth of the microflask by soft rubber tubing sleeve *B*. Cold-finger condenser *C* slips easily into either of the upper openings, the vacant one being closed by cork *D*. Set up as shown, refluxing occurs; mere interchange of the positions of *C* and *D* allows distillation to be carried out. If fractionation is desired, the cork may carry a 6-in. thermometer. The design may be readily adapted to incorporate standard ground joints. Water is carried to and from the condenser by leads of $\frac{1}{8}$-in. thin-walled rubber tubing. The leads pass through holes in the vertical panel and terminate in connections of brass tubing which are mounted near the back of the block.

Trials showed the block-type unit to be of considerable value in the hands of experienced workers. To students beginning identification work, however, the extreme compactness proved to have negligible advantages and it soon became apparent that a simpler, more flexible arrangement would be better for intro-

ductory work. A box-type set of apparatus, on the lines of that in use for small-scale preparative work (*8*), was therefore designed and has proved very satisfactory.

The box, which is lidless, numbered, and designed to stack in tiers of a dozen or so, is constructed mainly from 2 × $^3/_8$-in. hardwood strip as previously described (*8*). The arrangement of the partitions is shown in Figure 4. Drilled block *E*, the dimensions of which are $3^1/_2 \times 3 \times 1^5/_8$ in., is an easy fit in one portion of compartment *I* and enables micro test tubes, receivers, etc., to be supported when necessary. Sharing this compartment is heating unit *F*, which, like *E*, may either be used in place in the box or lifted out on to the bench top.

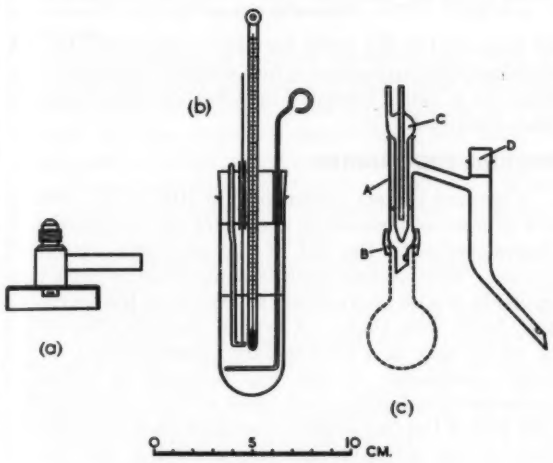

Figure 3. Details of Apparatus

(*a*) microburner; (*b*) melting-point apparatus; (*c*) "reflux-or-distill" attachment.

The heating unit, which is constructed from a wood block of the same dimensions as the test-tube block, is shown in Figure 5. To eliminate risk of scorching, the walls of the U-shaped burner space *G* are lined with tin plate or thin sheet aluminum, while a 2-in. strip of similar material forms the top plate. The latter, which has a $^3/_4$-in. central hole, is secured by bending the ends downward and tacking them to the sides of the block. Burner tube *H* is a 4-in. length of $^1/_8$-in. outside diameter brass or copper tubing which is bent twice at right angles as shown at (*a*). The wingtop jet is made by crushing the end of the shorter arm, after inserting a slip of thin sheet metal (*e. g.*, a fragment of a safety razor blade) to prevent complete closure. To permit attachment of the gas connection, the upper end of hole *I*, through which the longer arm of the burner tube passes, is opened out to $^5/_8$-in. diameter for a depth of about $^1/_2$ in. A recess *J*, running from the lower end of *I* to the burner space, enables the burner tube to be held in place by a single screw, so that the center of the hole in the top plate is vertically above the burner.

Whereas the 50-ml. water bath is heated merely by standing it on the top plate, flasks, etc., require additional support. This is provided by the detachable spring clamp shown at (*b*), the stem of which slips into blind hole *K*, which is about 1 in. deep. This clamp is a "Terry clip" which is screwed or soldered to the end of a $3^1/_2$-in. length of $^1/_8$-in. nickel or brass rod, the latter being bent at right angles as shown.

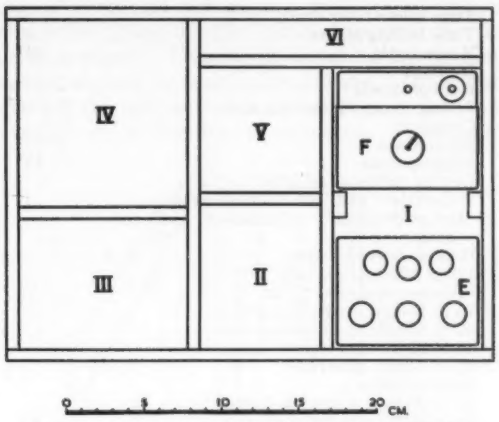

Figure 4. Containing Box for Identification Apparatus

In addition to the block and heating unit, each box contains the following apparatus:

No.	*Part*	*Compartment No.*
2	2-ft. length $^1/_8$-in. black rubber tubing (for water)	I
1	Ditto, red (for gas)	
2	Adapters for tubing	II
1	Sodium needle	
1	Tweezers	
1	Tube litmus squares	

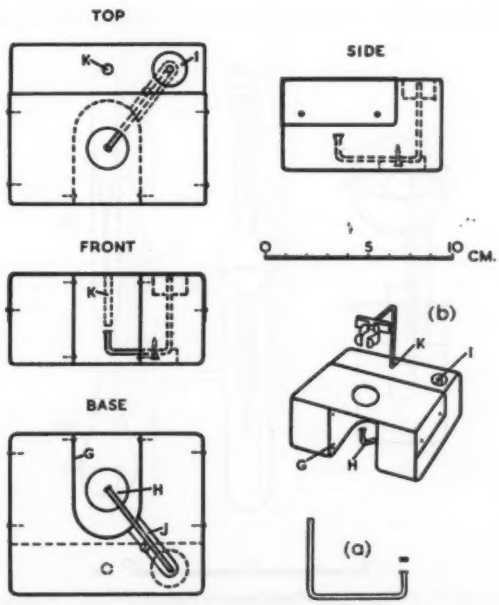

Figure 5. Heating Unit with Detachable Spring Clamp

1	Tube micro filter discs	
1	Tube boiling stones	
1	Water bath	III
1	Ice bath	
2	Rubber bands	
1	Spring clamp for heating unit	
6	Corks	
2	Microflasks	
1	Microspatula	IV
1	Drying tube and adapter	
1	Willstätter "nail" filter and receiver	
1	"Reflux-or-distill" attachment and condenser	
1	Rubber sleeve for same	
1	120 × 12-mm. test tube	
2	Microscope slides	V
1	75 × 15-mm. crystallizing tube	
2	40 × 15-mm. crystallizing tube	
2	45 × 12-mm. receivers	
3	60 × 3-mm. glass rods	
3	Ignition tubes	
2	75 × 10-mm. micro test tubes	
1	Tube melting-point capillaries	VI
1	Teat pipet (*9*)	
1	6-in. thermometer, 0–200°C., in case	

The water bath is a 50-ml. beaker provided with fused-on "ears." Crystallizing tubes may be conveniently supported by thrusting them within a rubber band stretched between the "ears," as shown at (*a*) in Figure 6. The ice bath is a 25-ml. beaker, similarly modified. A dissecting needle with a cut-down handle fitting stopper-wise into the mouth of a micro test tube as shown at (*b*), is used for handling sodium.

The drying adapter for use with the 25-mm. diameter Willstätter "nail" filter is merely a rubber teat with part of the bulb removed, as shown at (*c*). After the product on the filter disc has been washed under light suction, the adapter is forced over the mouth of the funnel, as shown at (*d*). The drying tube is then inserted and the suction maintained for a further five minutes or so.

Other apparatus either requires no special description

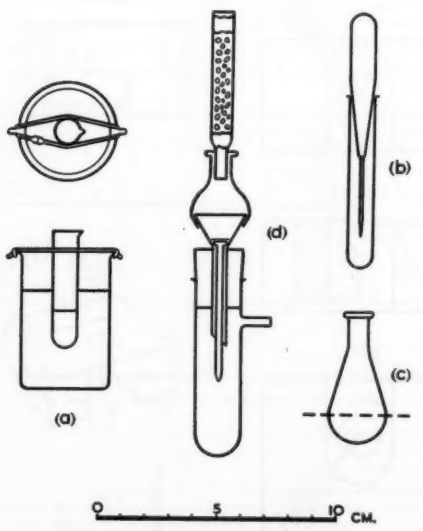

Figure 6. Miscellaneous Apparatus

(*a*) water bath; (*b*) sodium needle; (*c*) and (*d*) drying adapter.

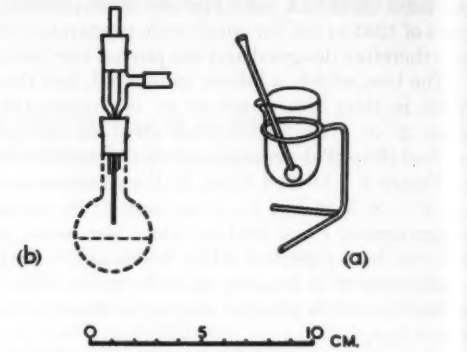

Figure 7. (*a*) Miniature Pestle and Mortar; (*b*) Arrangement for Taking off Solvent

or is as used in the outfit for preparative work (*8*). A melting-point apparatus is not actually included in the box, but is issued mounted on a heating unit similar to that described.

TYPICAL PROCEDURES

A student project commenced in 1952 is the working out of a set of instruction sheets for the preparation of derivatives with the aid of the apparatus described above. Most of this work is being done by part-time students, whose interests are as diverse as the textbooks they bring with them. A typical example (the details of which may of course undergo improvement as the work continues) is the identification of aromatic hydrocarbons, halides, and ethers as their sulfonamides. The first of the two stages in this process is the preparation of the sulfonyl chloride, involving the use of chlorosulfonic acid (*2*, *3*). Handling of this unpleasant reagent is of course supervised by the instructor. To minimize fuming, a dry teat pipet made by pulling out a short length of 7-mm. outside diameter glass tubing into a fine jet about 80 mm. long is used. The wetted area exposed to the atmosphere is thus made as small as possible. The procedure is as follows:

Dissolve 4 drops of anisole in 1 ml. of dry chloroform contained in a 40 × 15-mm. crystallizing tube supported in an ice bath. *Cautiously* add 10 to 12 drops of chlorosulfonic acid and allow to stand for 3 to 5 minutes, stirring occasionally until the initial evolution of hydrogen chloride ceases. Remove from the ice bath and leave for 30 minutes. By means of a teat pipet, *cautiously* transfer the reaction mixture to 5 g. of crushed ice contained in a 75 × 15-mm. crystallizing tube, using a few drops of chloroform to complete the transference. As soon as the ice melts and two layers separate, pipet off and reject the bulk of the aqueous (upper) layer. Use 1 ml. of water to wash the chloroform layer, then transfer the latter to a microflask, using a few drops of chloroform to complete the transfer. Take off the solvent by gently warming in an air stream. Add 0.5 ml. of water and 1 ml. of concentrated ammonium hydroxide (sp. gr. 0.88) and reflux for 10 minutes. Allow to cool, add 2 ml. of water and stand in the ice bath for about 5 minutes.

Filter off the sulfonamide, dissolve in 2 or 3 drops (minimum) of hot ethanol, and add water in drops until the first permanent turbidity appears. Clear by rewarming, adding a tiny drop of ethanol if necessary, and allow to cool, finishing off in ice. Filter off the crystals, continue suction for 5 minutes after attaching the drying tube and determine the melting point of the derivative.

Certain pieces of apparatus in less frequent use are not included in the standard set, but are either issued as required or, quite frequently, made by the student. For example, the micropestle and mortar shown at (*a*) in Figure 7 is easily constructed from a heavy-quality test tube and a piece of glass rod (*5*). A simple wire stand allows the device to be conveniently supported on a balance-pan for the direct weighing of materials.

Small quantities of volatile solvents, etc., may be rapidly removed by heating in a water bath and using the teat pipet to deliver a series of puffs of air onto the surface of the liquid. Larger quantities may be evaporated off either under vacuum or in an air stream, using the arrangement shown at (*b*) in Figure 7. Where the volatile substance is required, the "reflux-or-distill" device is of course used.

The saponification of simple esters and the identification of ethanol, etc., in the dilute distillate, by oxidation to the aldehyde and its conversion to the 2,4-dinitrophenylhydrazone may be carried out as previously described (*7, 8*). Alternatively, the alcoholic distillate, obtained by the use of the "reflux-or-distill" device, is treated in the micro air-flow apparatus shown in Figure 8. Oxidation vessel *L* is a micro test tube in the wall of which a 1-mm. hole *M* is blown. Use of a microblow-pipe[1] made from copper foil and a steel washer (*6*) renders this operation very simple. Since the total volume of air drawn through the apparatus need not exceed 20 ml., an ordinary buret filled with water and carrying the simple attachment shown at (*a*) makes a satisfactory aspirator. Procedure is as follows:

Transfer 1 to 2 drops of the distillate to the oxidation vessel of the air-flow apparatus. Add 4 drops each of 5 per cent potassium dichromate solution and 4 *N* sulfuric acid. Place about 2 ml. of saturated 2,4-dinitrophenylhydrazine solution in 2 *N* hydrochloric acid in the precipitation vessel and assemble the apparatus. Apply gentle suction to the side tube, so that a flow rate of about one bubble of air per second is maintained. Using a microflame, gently heat the liquid in the oxidation vessel to incipient boiling; to prevent spurting, apply the flame a little below the surface of the liquid, rather than at the bottom of the tube. When the liquid darkens, roughly double the bubbling rate, when precipitation of the 2,4-dinitrophenylhydrazone should occur.

Filter off the precipitate on a Schwinger filter, rinsing out the precipitation vessel with a few drops of 2 *N* hydrochloric acid. Wash the precipitate with a few drops of water and transfer to a small crystallizing tube, using a few drops of ethyl alcohol to rinse the funnel and filter paper. Dissolve in about 0.5 ml. (minimum) of ethyl alcohol by heating on a water bath, close the mouth of the tube with a slotted cork and allow to cool, finishing off in ice for 10 minutes. Filter off the crystals, wash with 2 drops of cold ethyl alcohol and continue suction for 5 minutes after attaching a drying tube. Determine the melting point of the derivative.

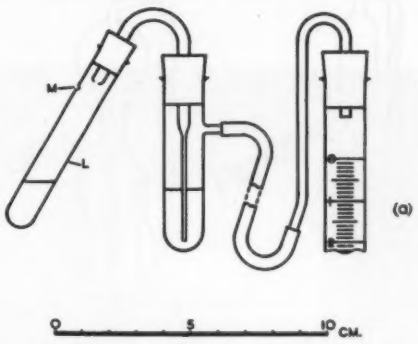

Figure 8. Micro Air-flow Apparatus

The Schwinger filter, so useful when the amount of solid is small, is shown in its usual form at (*a*) in Figure 9. It has two minor disadvantages: on assembly, the tiny filter disc *N* may become displaced, and the fault being obscured by rubber sleeve *O*, may escape notice until the filter is used; and unless it is large, the size of the column of solid collected cannot be observed until

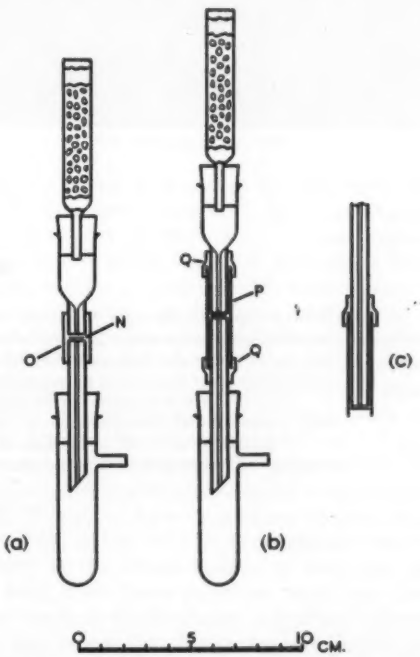

Figure 9. (a) Schwinger Filter; (b) Improved Form of Microfilter; (c) King Filter

[1] Exhibited at the International Congress on Analytical Chemistry, Oxford, England, September, 1952.

the funnel is dismantled. An improved form, which has been in use for some months, is shown at (*b*). The parts of the filter stem are a snug fit in glass tubing guide *P* and are secured by rubber tubing sleeves *Q*. Not only may the filter disc and the collected solid be

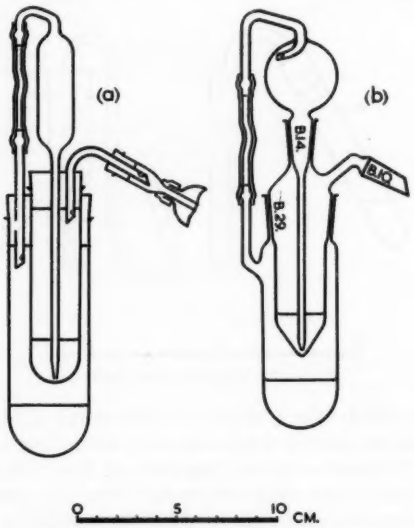

Figure 10. Steam Distillation Apparatus

easily observed, but the filter assembly is given considerable rigidity. On removing the funnel portion and upper sleeve and then pushing the lower portion of the stem further into the glass guide as shown at (*c*), the device becomes a King filter (*1*), so useful for inverted filtration.

Although compact, the Pozzi-Escot steam distillation apparatus (*4*) is neither easy to clean nor immune from sucking back. Although it will increase the volume of distillate, a steam bypass (*8*) may be incorporated to eliminate sucking back. An easily assembled form of apparatus not subject to either disadvantage and giving a very good performance is shown at (*a*) in Figure 10. The steam jet is constructed from an old 20-ml. pipet, the bulb of which is wound with asbestos string to minimize condensation. A design incorporating standard ground joints is shown at (*b*). The short rubber connecting tube not only permits easy assembly and dismantling but also allows the assembled apparatus to be safely picked up by the bulb.

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NEW FILMSTRIPS

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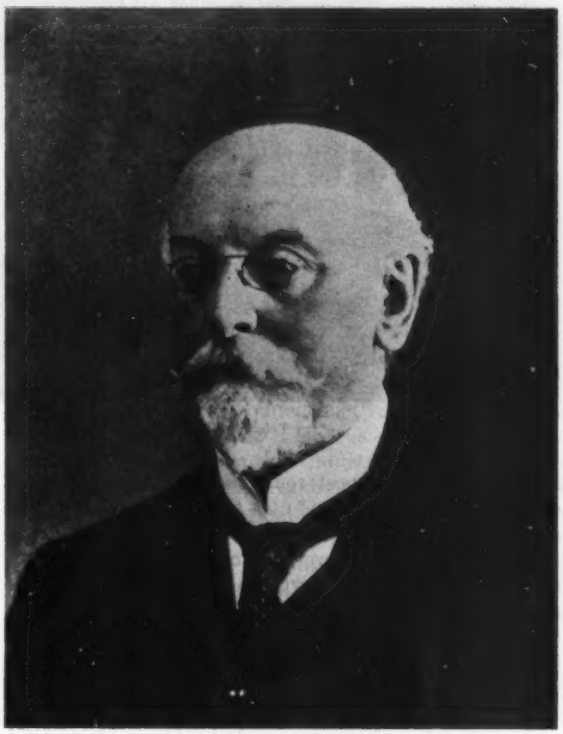
JAMES EMERSON REYNOLDS[1]

DESMOND REILLY
Westvaco Chemical Division, Food Machinery and Chemical Corporation, New York, New York



James Emerson Reynolds

James Emerson Reynolds was born at Booterstown, near Dublin, Ireland, on January 8, 1844.[2] His father, James Reynolds, was a practicing physician and also a moderately successful amateur playwright. It was intended that Emerson Reynolds, as he was usually known, should become a doctor too, and as a youth he became an assistant to his father. At the age of 21 he qualified as a licentiate of the Edinburgh College of Physicians and Surgeons, and set up in a practice for a short time in Dublin. However, on his father's death a few years later, he definitely abandoned medicine and devoted himself to chemistry.

His interest in chemistry dated back to his high-school days when he fitted out a home laboratory. He was entirely self-educated in chemistry and never attended a systematic course of college instruction in either theoretical or practical chemistry. When he was 17 years of age he published two papers in the British *Chemical News*. The first was "On the oleaginous matter formed on dissolving different kinds of iron in dilute acids,"[3] and the second was "On a new process for photographic printing."[4] A year later the same journal published a communication by Reynolds on the "Oxalates of iron."[5] The next year he published three more papers in *Chemical News* and two in the *Journal of the (Royal) Dublin Society*.[6] Though these early papers were of no special merit or great originality, they are certainly remarkable as the work of a self-taught young chemist, wholly unguided and with limited means. His work was undoubtedly carried on under considerable difficulties, and as it was presumably regarded as an interruption of his medical studies, he probably received little encouragement at home.

These early papers also serve to show the range of his interests and his grasp of contemporary scientific developments. Spectrum analysis, the subject of one of these early papers, was only in its infancy at that date. It is probable that Reynolds' practical interest as well as his later work in this field resulted from his hearing popular lectures given at the (Royal) Dublin Society by Sir Henry Roscoe and Sir William Huggins.

Reynolds first had access to a fairly well-equipped chemical laboratory in 1867 when he was appointed keeper of minerals at the National Museum in Dublin. The subject matter of many of his papers from then on, such as formation of dendrites, manganese ores, phosphoric acid in minerals, classification of silicates, notes on Irish rutile and the feldspars, boron minerals, and mineralogical tables, owed much to his museum background. In addition, the interest such work aroused in him in the chemistry of silicon led him to publish many papers through the years on the silicic acids, silicon halides, and silico-organic compounds.[7]

In 1868 Reynolds became analyst to the (Royal) Dublin Society, and in 1870 he was appointed professor of chemistry at the Royal College of Surgeons, Dublin. He held both these positions until his election in 1875 to the chair of chemistry in Dublin University, where he succeeded Dr. James Apjohn (1796–1886),

[1] Presented to the Division of History of Chemistry at the 123rd Meeting of the American Chemical Society, Los Angeles, March 17, 1953.

[2] Thorpe, T. E., *J. Chem. Soc.*, **117**, 1633–7 (1920).

[3] *Chem. News*, **4**, 4–5 (1861).

[4] *Ibid.*, p. 304.

[5] *Ibid.*, **5**, 16–8 (1862).

[6] "On the economical preparation of sulphocyanide of ammonium," *ibid.*, **8**, 14–5 (1863). "On the numerical nomenclature of spectral lines," *ibid.*, p. 59. "On the detection of hyposulphite of soda," *ibid.*, pp. 283–4. "Wood spirit and its detection," *J. Dubl. Soc.*, **4**, 126–30 (1863). "Note on pure methylic alcohol," *ibid.*, pp. 131–2.

[7] *J. Chem. Soc.*, **51**, 202–7, 590–2 (1887); **53**, 853–64 (1888); **55**, 474–82 (1889); **61**, 453–8 (1892); **77** (Pt. 2), 836–9 (1900).

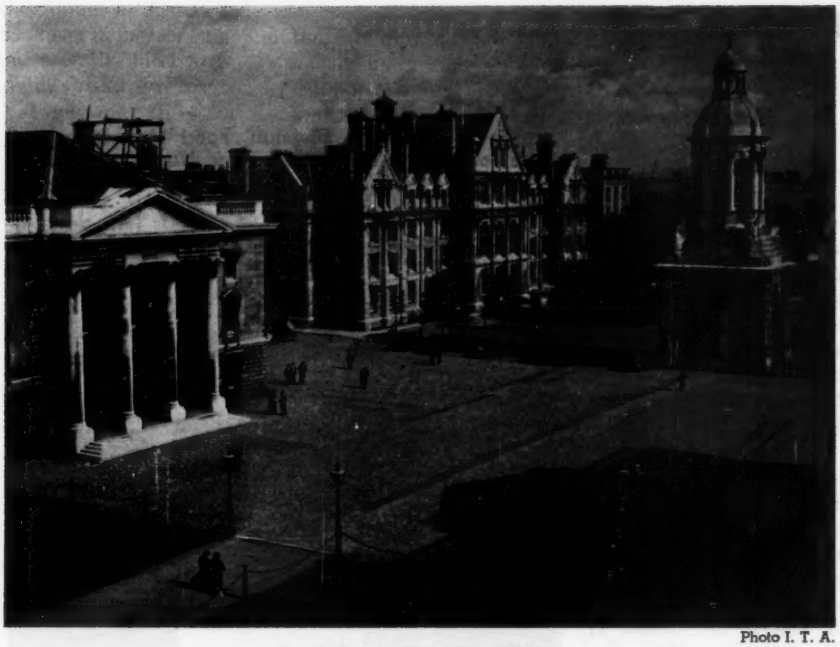


Photo I. T. A.

Trinity College, University of Dublin

a notable scientist best remembered for his work on dewpoint determinations.[8] At that date Reynolds had a considerable practice as a consultant and public analyst. He was interested in subjects relating to medical chemistry and hygiene and was co-author of a "Manual of Public Health for Ireland." He was also responsible for analytical work on Dublin city water supplies, and worked, as many Irish chemists have before and since his time, on the greater utilization of Irish peat.

An interesting discovery made by Reynolds in 1871 was that of a colloidal derivative of mercury and acetone[9] which originated from his experiments on wood-spirit. It was the first colloidal derivative of mercury to be announced, and it formed the basis for a sensitive test for acetone, a test still known as Reynolds' test. The neutral solution of this compound $(C_3H_6O)\cdot 3HgO$, prepared by dialysis, later found use as an antiseptic dressing in surgery where no ordinary mercurial solution could be used.

In Dublin University where he spent 28 years Reynolds proved to be a good lecturer and painstaking teacher, though not of the popular type as he was a strict disciplinarian and had a rather precise and dry manner. He was a pioneer in the use of experiments and demonstrations for lecture illustrations. He kept constantly abreast of new developments (as for instance those concerned with the doctrine of periodicity) and worked these into his courses. He was one of the first to introduce quantitative work into the early training of chemistry students, and developed his system in an original text in four volumes, "Experimental Chemistry for Junior Students," a work which was widely and well received.

The best known of Reynolds' contributions to organic chemistry is his discovery of thiourea. As mentioned earlier, one of his first papers from his home laboratory was on ammonium sulphocyanide (ammonium thiocyanate). On heating this salt to a few degrees above its melting point, dissolving the product in water, and allowing the concentrated solution to stand, he obtained a substance which crystallized in silky needles. The true nature of this substance escaped him for a time, but he eventually designated it as an "isomeride of sulphocyanogen," under which title he communicated a short paper to the *Journal of the (Royal) Dublin Society*.[10] A further paper appeared in the *Journal of the Chemical Society* soon afterwards, and was quickly reprinted in various European periodicals.[11] This was a remarkable discovery for a chemist in his early twenties, especially as men of the caliber of Liebig and Hofmann had failed to isolate thiocarbamide. Though the preparation is analogous to the Wöhler synthesis of urea by the rearrangement of ammonium cyanate, higher temperatures are required and the equilibrium is less favorable for the thio compound, yield being of the order of 28 per cent at 140°.[12] The mixture at equilibrium contains the complex $SC(NH_2)_2$, $(NH_4SCN)_3$, which melts at 105–106°, the eutectic point of the system.

Much of the subsequent work on the structure and chemistry of thiourea and of its substituted compounds came from Reynolds and his associates in Dublin University.[13] A standard method of iodometric estimation of thiourea was devised by this group,[14] and later an important paper appeared from the group on the dynamic isomerism of the thiourea-ammonium thiocyanate system in which it was shown that the reversion of

[8] REILLY, D., "Three Centuries of Irish Chemists," Cork University Press, Ireland, 1941, p. 21; FLEETWOOD, J., "History of Medicine in Ireland," Browne and Nolan, Dublin, 1951, p. 97.

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[11] *J. Chem. Soc.*, 7, 1–15 (1869); *Anal. Chem. Pharm.*, 150, 224–41 (1869); *Anales de Chimie*, 19, 441–5 (1870).

[12] KAPPANNA, A. N., *Quart. J. Indian Chem. Soc.*, 4, 217–28 (1927); *Chem. Abstracts*, 21, 3526 (1927).

[13] FEARON, W. R., "Obituary of E. A. Werner, 1864–1951," *J. Chem. Soc.*, 1952, 2947–52.

[14] REYNOLDS, J. E., AND E. A. WERNER, *J. Chem. Soc.*, 83, 1 (1903).

thiourea begins about 135°; the complex $(SCN_2H_4)_3$, NH_4SCN accumulates in the liquid phase below 140°; and the change in both directions is unimolecular.[15]

Reynolds was among the first to try to settle the true portion of the element beryllium (glucinum) in the periodic series and to establish its valency and atomic weight. For many years the valency of beryllium had been a subject of controversy. Berzelius and other early workers had finally leaned to the view that the element was trivalent. Early work on the specific heat of the element had favored the trivalency hypothesis but the data were by no means unequivocal because (1) results were discordant owing to the use of the impure metal; (2) the specific heat varies considerably with the temperature; and (3) the elements with low atomic weights often deviate so much from Dulong and Petit's rule that the application of the rule is of little value as a criterion.[16]

Much work had been concentrated on this question of the specific heat of the beryllium partly because of its value in determining the atomic weight of the element and partly because of its abnormal value at ordinary temperatures, as is the case with boron, carbon, and silicon. Reynolds found the specific heat to be 0.642 at 100°.[17] L. F. Nilson and O. Pettersson, however, calculated the specific heat of the pure metal to be between 0.3950 and 0.5055 depending on the temperature range.[18] Reynolds attributed the difference between his results and those of Nilson and Pettersson to be due to their using crystalline metal, while he used amorphous. Actually the metal he prepared was far from pure, and these impurities required a very uncertain correction factor. It was not established until a later date that only at very high temperature did atomic heat values approximate those required by the Dulong and Petit rule.

The work of T. S. Humpidge in 1885[19] showed that the specific heat remains practically constant at 0.62 at temperatures between 400° and 500°, the application of the Dulong and Petit rule then favoring the trivalency of the element. Reynolds' views of the question of the true place of beryllium in the atomic table and of its valency[20] were also borne out later by determinations of the vapor density of the chloride and other salts, which all indicated the trivalency of the element.

[15] ATKINS, W. R. G., AND E. A. WERNER, *J. Chem. Soc.*, **101**, 1167–78 (1912).

[16] MELLOR, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1946, Vol. 4, pp. 213, 219.

[17] *Phil. Mag.*, **3**, 38–42 (1877).

[18] *Ber.*, **17**, 987 (1884).

[19] *Proc. Roy. Soc.*, **38**, 188 (1885); **39**, 1 (1886).

[20] *Ibid.*, **35**, 248–50 (1883).

Reynolds resigned from his Dublin post in 1903, being succeeded by E. A. Werner.[21] He moved to London where he continued his experimental work at the Davy-Faraday laboratory and ultimately fitted up a private laboratory at his home in Kensington. His last published paper, "On the synthesis of silical cyanide and of a feldspar,"[22] described the synthesis of a silicon compound of aluminum and calcium, a calcium silicalcyanide $CaSi_2Al_2$, analogous to calcium cyanide. Reynolds' view had long been that in nature aluminum appeared to have a relationship to silicon in inorganic compounds rather like that of nitrogen to carbon in organic materials.[23] On oxidation, Reynolds' silicalcyanide yielded a substance of the composition of anorthite ($CaO.Al_2O_3.2SiO_2$), with the properties of the naturally occurring mineral. Nearly half a century of chemical work had brought him from his early mineralogical studies in Dublin to his last work involving the synthesis of the mineral anorthite in his London home.

Reynolds was a prominent figure for many years in various chemical organizations. He held three three-year terms as vice-president of the Chemical Society, and was the Society's president from 1901 through 1903. He was elected a Fellow of the Royal Society in 1880, served on its council for two years, and was a vice-president in 1901–02. He was an original member of the Society of Chemical Industry, of which he became President in 1891, presiding over the only Annual Meeting of the Society held in Ireland, and reading an address on the world's supply of coal, peat, and petroleum in Dublin at that meeting.[24] He was president of the chemical section of the British Association at their Nottingham meeting in 1893, reading an address on the chemistry of silicon compounds.[25]

Reynold's wife, Jane Elizabeth Finlayson, was the daughter of a canon of Christ Church Cathedral, Dublin, and they had two children. In his later years, as with a number of chemists, his eyesight gradually failed, though he remained mentally alert until the last. He had a serious accident shortly before his 76th birthday, fracturing a rib. This was followed by a slight stroke from which he never fully recovered. He died suddenly on February 17, 1920, at his home in Kensington, England.[26]

[21] FEARON, W. R., *op. cit.*

[22] *Ibid.*, **A88**, 37–48 (1913).

[23] WERNER, E. A., "James Emerson Reynolds," *J. Soc. Chem. Ind.*, **39**, 122R (1920).

[24] *J. Soc. Chem. Ind.*, **11**, 571–7 (1892); WHEELER, T. S., *J. Roy. Inst. Chem.*, **77**, 66 (1953).

[25] *Brit. Ass. Rep.*, **1893**, 708–15.

[26] Reynolds' papers to the year 1900 are listed in the *Royal Society Catalogue of Scientific Papers*, as follows: **5**, 181 (1871); **8**, 739–40 (1879); **11**, 161–2 (1896); **18**, 160 (1923).

THE SCIENCE FAIR IN SOUTHERN MINNESOTA

LEONARD A. FORD
State Teachers College, Mankato, Minnesota

Although science fairs have been fairly common in the metropolitan centers in the east little has been done in the midwest to increase interest in science by this method. Science teachers in Minnesota high schools teach more than one science and most of them also have extracurricular duties. This gives them little opportunity to work on projects, and as a result they have little interest in activities that are not directly related to their teaching. To give teachers in the area an added interest in science, and with a view to improving their teaching and thus stimulating their students, the author was instrumental in organizing a group of high-school teachers shortly after the war. This group, known as "Southern Minnesota Science Teachers League," had regular meetings at Mankato State Teachers College with elected officers. Because participants in these meetings were sometimes separated by as much as 150 miles it was not an easy matter to keep the group active in view of the rugged Minnesota winters.

In the spring of 1950 the author proposed a science fair to the science teachers, to be held the following year. Since it was a completely new idea it did not meet with a ready response but the teachers agreed to participate. Fourteen schools were represented at the first fair in 1952 and about 500 students were registered. A featured speaker, Dr. C. A. Owens of the Mayo Clinic at Rochester, Minnesota; a chemical magic show by college students; college and high-school science exhibits; and a few local industrial exhibits and science movies comprised the day's activities. The enthusiasm and interest created by the first fair helped to attract 700 students to the 1953 fair with entries from 30 schools.

Publicity by daily and weekly newspapers, the radio, and information bulletins by the author helped to create interest in the fair. The mailing list of science teachers in the smaller towns was obtained from the office of the Minnesota Education Association. Information directed to the teachers gave the names of industrial exhibitors, types of student projects, and name of the featured speaker, and expressed the hope that the teacher would have student projects to exhibit at the fair. Teachers and their students were urged to come, even if they had no exhibits to display. Information about the fair was presented over a period of three or four months.

Since the number of exhibitors at the first fair was relatively small the author planned a "chemical magic" show which proved to be an entertaining feature. The event was conducted by five college students who had rehearsed each of the demonstrations many times previously. The chief magician, dressed in a tuxedo and top hat, directed the work of the others. To increase the effect the experiments were accompanied with humorous stories. Since the purpose of the show was to entertain as well as to instruct, the performers made up fantastic explanations which accompanied each experiment. It was noted that these stories became more exaggerated with each performance, as the demonstrator gained confidence and skill. Delayed reactions, explosions, colored fires, candles which light mysteriously, cold fire, ammonia fountains, solid alcohol, and Pharaoh's serpents indicate the nature of the demonstrations. Rehearsal of each experiment until it was "foolproof" was essential. This meant that the student had to repeat the experiment many times and carefully work out his story so that the audience would enjoy this feature of the fair. During the second fair the magic show again proved to be popular and it was necessary to turn away many students at each performance.

Exhibits and demonstrations by 19 industrial and governmental concerns played an important part in the second fair. Included were concerns from different parts of the state. Some of these were U. S. Steel, Minneapolis-Honeywell Regulator, The Hormel Institute, Continental Can, and the State Department of Agriculture. These exhibits showed the part that science plays in industry today. The fair was a new venture to these exhibitors, who were highly pleased with the interest that high-school students showed in their exhibits and demonstrations.

Student exhibits were placed in science laboratories and those students that cared to do so gave oral explanations or demonstrations of their exhibits at a demonstration desk. Interest in the exhibit was increased when the student was given an opportunity to tell about his work, how it was prepared, and what it was intended to show. Exhibits and demonstrations by junior and senior high-school students were divided into areas of physics, mathematics, chemistry, biology, general science, and photography. The featured speaker, Dr. A. F. Voight of the Institute of Atomic Research, Ames, Iowa, addressed the group at a general assembly on "Peace-time Uses of Atomic Energy."

Cost of operation of the fair was held to a minimum, since funds were not available from the college for events of this type. However, award ribbons and the expenses of a speaker were met by industry and a fee of $3.00 from each participating school. Red ribbons were awarded to all exhibitors and blue ribbons for outstanding exhibits. Slide rules, handbooks, and other prizes donated by industry were given for the best exhibits. Twenty memberships in the Minnesota Junior Academy of Science were also awarded.

EXPERIMENTS IN PAPER PARTITION CHROMATOGRAPHY WITH TAGGED MATERIAL

FAUSTO W. LIMA
Instituto Biológico, São Paulo, Brazil

THE series of papers by Williams, Hamill, and Schuler (*1*) on laboratory exercises in nuclear chemistry and the one by Trumbore and Rogers (*2*) on chromatography suggested some experiments in inorganic chromatography using radioactive isotopes, which could be of instructional value on various topics in radiochemistry.

The experiments to be described below are simple and inexpensive and can be performed in any laboratory with ordinary counting equipment and X-ray film. Although the radioactive material used is of long half-life (Ra D, E, F), the danger of contamination is practically non-existing since the handling of radioactive solutions is required only for the preparation of the chromatograms.

The experiments will illustrate the following topics: the behavior of radioactive substances in the absence and in the presence of macro amounts of isotopic carrier; the technique of radioautography; the determination of Rf values for bismuth and polonium at tracer level; the determination of the half-life and the construction of absorption curves for a beta-emitter isotope; the efficiency in counting a pure alpha emitter and a beta emitter; genetic relationships as in the case of Pb^{210}, Bi^{210} and Po^{210}; the construction of a growth curve and the study of secular equilibrium; and the counting of beta radiation when beta and alpha particles are being emitted by the same material, or of beta radiation of different energies.

Ra D or Pb^{210} is a radioactive isotope of lead which is produced by the disintegration of radon. Ra D has a half-life of 22 years and emits beta minus particles of maximum energy 0.0255 m. e. v. giving rise to Ra E, an element of atomic number 83 (hence an isotope of bismuth), and mass number 210; Bi^{210} is also radioactive and has a half-life of 5.0 days; it emits beta minus particles of maximum energy 1.17 m. e. v. and as a result transforms itself into an element of atomic number 84 and mass number 210. This element 84 is an isotope of polonium, has a half-life of 140 days and emits alpha particles of energy 5.298 m. e. v. giving rise to an element of atomic number 82 and mass number 206, which is a stable isotope of lead. The disintegration scheme is

$$_{82}Pb^{210} \xrightarrow{\beta^-} {}_{83}Bi^{210} \xrightarrow{\beta^-} {}_{84}Po^{210} \xrightarrow{\alpha} {}_{82}Pb^{206}$$

As is known (*3*, *4*), the decay of Pb^{210} and the growth of Bi^{210} and Po^{210} may be described by the relations

$$a_1 = a_1^0 e^{-\lambda_1 t} \qquad (1)$$

$$a_2 = \lambda_2 a_1^0 \, (e^{-\lambda_1 t} - e^{-\lambda_2 t})/(\lambda_2 - \lambda_1) \qquad (2)$$

$$a_3 = \lambda_2\lambda_3 \, a_1^0[e^{-\lambda_1 t}/(\lambda_2 - \lambda_1)\,(\lambda_3 - \lambda_1) + e^{-\lambda_2 t}/(\lambda_1 - \lambda_2)\,(\lambda_3 - \lambda_2) + e^{-\lambda_3 t}/(\lambda_1 - \lambda_3)\,(\lambda_2 - \lambda_3)] \qquad (3)$$

a_1, a_2, and a_3 are the activities of lead, bismuth, and polonium, respectively; the superscript zero refers to the activity at time zero. It is supposed that no bismuth or polonium existed at time zero, *i. e.*, the experiment started with pure Pb^{210}.

Since the energies for beta particles of Pb^{210} and Bi^{210} are quite different, it will be possible to observe, in a Geiger counter, the activity due to bismuth only, by interposing between counter and source an absorber for the lead's radiation. In the experiments to be described an aluminum absorber with a thickness of 11 mg. per sq. cm. was used; this absorber will also cut out the alpha rays from polonium.

If Bi^{210} and Po^{210} are separated from Pb^{210} by the chromatographic procedure to be described, it will be possible to check equation (2) by counting the Pb^{210} preparation free from Bi^{210} and Po^{210}; it will be noticed that the activity of the lead preparation will grow with time up to a point where it will be practically constant; actually the activity will decay with the half-life of Pb^{210}. However, since this half-life is fairly large compared with the time of observation, the decay is practically negligible. This situation is known as "secular equilibrium," and in this condition the daughter activity is equal to the parent activity, *i. e.*, $a_1 = a_2$. The time t_e needed to reach this status is obtained by equating (1) and (2); thus one gets

$$t_e = \frac{1}{\lambda_2 - \lambda_1} \ln \lambda_2/\lambda_1 \qquad (4)$$

By substituting the corresponding values for Pb^{210} and Bi^{210} for λ_1 and λ_2, t_e turns out to be 53.2 days.

PROCEDURE

A saturated solution of lead nitrate, tagged with Ra D, E, F, acidified with nitric acid to a pH of about 2.5, was used. The activity of the solution was determined by pipetting 0.1 ml. into an aluminum sample pan, drying it under an infrared heat lamp, and counting. A 3.2-mg. per sq. cm. mica end-window Geiger counter was used. To count only particles from the Ra E, an aluminum absorber of 11 mg. per sq. cm. was used to absorb the soft beta particles from lead and the alpha particles from polonium. The counting rate was then compared with counting rate of a uranium

standard of known activity. In this case, an aluminum absorber of 30 mg. per sq. cm. was used in order to absorb the soft beta radiation from UX_1, leaving only radiation from UX_2 to be counted. To correct both activities to counting rate with no absorber, an aluminum absorption curve was determined for the uranium standard and for the tagged lead nitrate, and both curves were extrapolated to zero absorber. The lead nitrate solution turned out to have an activity of 0.35 microcurie/ml.

Preparation of the Chromatograms. The technique for running the chromatograms was, essentially, the same one described previously in the literature (*2*, *5*, *6*, *7*).

Strips of Whatman No. 1 paper, 2.5 cm. in width and 40 to 50 cm. in length were used. A pencil mark was drawn in the middle of each strip at about 5 cm. from one end. The solution to be analyzed was applied at this mark from the tip of a micropipet. The amount of solution used was 0.01 ml.; the solution was applied slowly rather than all at once, so that a round spot not larger than 0.5 cm. in diameter was obtained.

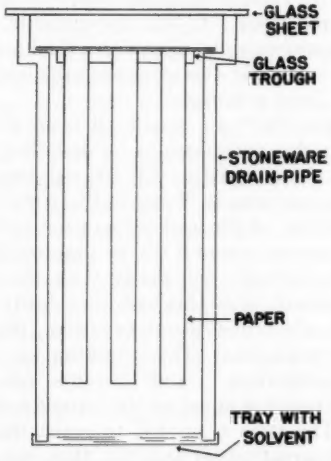

Figure 1 After Consden, *et al.* (*5*)

The end of the paper was fixed in a glass trough with a microscope slide; the spot with the solution to be analyzed was then at about 2 cm. from the edge of the trough. The trough with the paper was put in a vertical stoneware drain-pipe, which served as the chamber and at the bottom of which was a beaker with a mixture of water and the solvent (butanol saturated with a 3-*N* hydrochloric acid solution). The pipe was covered with a glass sheet. In this way the atmosphere in the drain-pipe was saturated with both components of the solution. The drain-pipe was 20 cm. in diameter and 80 cm. long. Such dimensions were found convenient so that three (or more) strips of paper could be used at a time, making experimental conditions the same for every set of three chromatograms. To prevent the atmosphere inside the pipe from becoming diluted by air the pipe could be placed over a circular tray, with diameter larger than the pipe, containing the water-solvent mixture; in this case the beaker mentioned before was not necessary.

After being placed in the chamber, the trough was filled with butanol saturated with a 3-*N* solution of hydrochloric acid and the glass sheet was replaced on top of the pipe, the edges of which were coated with vaseline. The apparatus is shown in Figure 1.

The chromatograms were left to run from 18 to 22 hours at room temperature and the strips of paper were then removed and dried in a stream of air.

Three chromatograms were made. In chromatogram No. 1 about 0.01 ml. of the tagged lead nitrate solution was placed on the extremity of the paper. A second chromatogram was prepared using the same solution as on chromatogram No. 1 plus 0.01 ml. of a non-tagged bismuth nitrate solution whose normality was 0.1. A third one was prepared using only non-tagged substances, *i. e.*, 0.01 ml. of a 0.1-*N* lead nitrate solution and 0.01 ml. of a 0.1-*N* bismuth nitrate solution. Notice that chromatogram No. 1 will give information on bismuth carrier-free, polonium carrier-free, and on lead with carrier; chromatograms No. 2 and 3 will give information on bismuth and lead at ordinary concentrations. After the chromatograms had been run and dried they were sprayed with sodium sulfide solution. On chromatograms No. 2 and 3 two black spots appeared.

At this point it is necessary to define an important symbol in chromatography, *i. e.*, Rf values. The Rf value is the ratio between the distance measured from the point where the material was initially placed to the spot where it stopped and the distance traveled by the solvent, also measured from the same starting point. Main factors that influence the value of Rf are temperature, saturation of the atmosphere with solvent vapor, acidity of original solution, and time of running of a strip.

The black spots mentioned appeared at Rf = 0 and Rf = 0.65. These Rf values are the ones reported by Lederer (*8*) for lead and bismuth. On chromatogram No. 1 only one spot appeared at Rf = 0; nothing appeared at Rf = 0.65 on this strip because bismuth is at tracer level and the solubility product of bismuth sulfide is not reached. In the case under study, Rf values were not rigorously the same and the values reported are the averages obtained from 15 experiments. However, in all experiments the spots were well defined and well separated and in no case was there superposition.

Preparation of the Radioautograms. The preparation of chromatograms Nos. 1 and 2 was repeated but they were not sprayed with sodium sulfide. Instead, after drying they were placed in close contact with a strip of medical X-ray film and left in the dark for five days. The films were then developed in Kodak D-19 and intensified with Kodak Chromium Intensifier In-4. In both strips of film three black spots appeared, at Rf = 0, Rf = 0.65, and Rf = 0.88. The spot at Rf = 0.65 was very weak and could be best observed by placing a white

sheet of paper behind the film instead of looking through it directly against light. The Rf values were compared with the ones on chromatogram No. 3 obtained by the spraying with sodium sulfide: the spots at Rf = 0 and Rf = 0.65 are lead and bismuth, respectively. The element at Rf = 0.88 will have to be characterized by its radioactive properties only, since no polonium at high concentration was used for comparison. The sequence of spots was in agreement with the one found, for the same isotopes, by Frierson and Jones (*9*).

An observation of the behavior of bismuth at ordinary concentrations and at carrier-free levels can be made by comparing the spots at Rf = 0.65 obtained on films corresponding to strips No. 1 and No. 2 with the black spot obtained on strip No. 3 by the reaction of bismuth with sodium sulfide. On strip No. 1 bismuth is at tracer level; on strips No. 2 and No. 3 it is at ordinary concentration since it was precipitated by sulfide ion. However, in all three chromatograms the Rf values were the same. This is to be expected if we adopt the view that cellulose acts as an inert support, in accordance with Consden, Gordon, and Martin (*5*), and that partition chromatography is analogous to equilibrium distribution between two immiscible solvents. For this last phenomenon it has been shown by Bonner and Kahn (*10*) that macro amounts of material and material at tracer levels follow the same distribution law.

Scanning of the Chromatograms. The determination of Rf values for lead, bismuth, and polonium can also be made with a Geiger counter, using an automatic device for scanning like the one of Müller and Wise (*11*), or by cutting the strips of paper in various parts of equal size from Rf = 0 to Rf = 1. In order to do this, chromatogram No. 1 was cut into pieces 1 cm. wide, thus producing various samples for counting. Rf values were then obtained by taking the middle of each piece as reference. A 3.2-mg. per sq. cm. mica-window Geiger tube was used and the sources were placed at a distance of 1 cm. from the window. The zone corresponding to Rf = 0 gave a high counting rate; from Rf = 0 to Rf = 0.60 the counting rate was only that due to background. From Rf = 0.60 to about Rf = 0.67 the counting rate increased with a maximum at Rf = 0.65. From Rf = 0.67 to Rf = 0.84 the counting rate was again of background level; at Rf = 0.84 it increased once more, giving a maximum at Rf = 0.88 and then decreased to background level up to Rf = 1. Counts at the maximum of Rf = 0.88 were much less than those at Rf = 0 and Rf = 0.65, indicating that there was a smaller amount of substance at Rf = 0.88 or that a weaker type of radiation was being emitted. Figure 2 gives the peaks obtained as well as the drawing of a chromatogram as it appears on the X-ray film; the counting was made after five days had elapsed since the development of the chromatogram.

Identification of the Isotopes. As a next step, the identification of the elements by their type of radiation was made. To identify the isotope of Rf = 0.65 an aluminum absorption curve and a half-life determination were run. The range was found to be 450 mg. per sq. cm., approximately; in a range-energy graph for beta radiations, as given by Williams (*3*), the corresponding energy for this range is 1.0 m. e. v. The half-life was 5.2 days, a value which is in fairly good agreement with the one obtained in one of the most recent determinations of the half-life of Ra E (*12*).

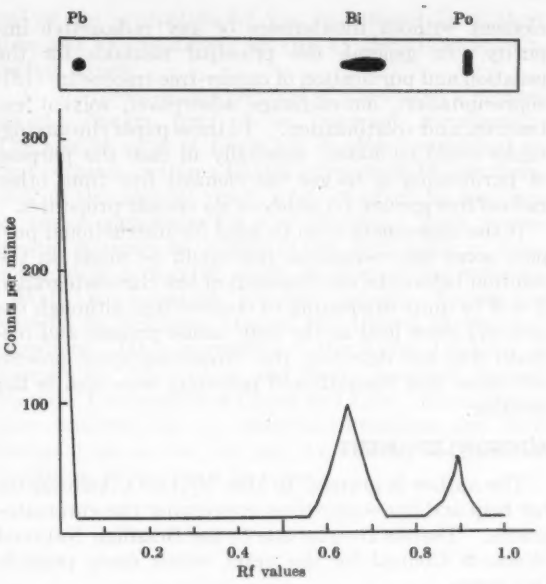

Figure 2. Scanning of a Chromatogram with Geiger Counter and Radioautogram on X-ray Film

That the isotope at Rf = 0.88 was an alpha emitter was verified by counting the sample placed at a distance of 1 cm. and of 6 cm. respectively from the window of the Geiger tube; at 1 cm. the activity was from 50 to 60 counts per minute on the various chromatograms; at 6 cm. no activity above background was detected. The half-life was determined and a value of 132 days was obtained, indicating that the isotope at Rf = 0.88 was polonium.

The determination of the activity at Rf = 0 will be used to illustrate the growth of a radioactive substance. At Rf = 0 there is practically only Pb^{210} when the chromatogram process is finished. A growth curve for Bi^{210} corresponding to equation (2) was made. In order to count only radiation from Bi^{210} an aluminum absorber of 11 mg. per sq. cm. was placed between the sample and the Geiger counter. A typical exponential growth curve was obtained. The confirmation that this activity was owing only to Bi^{210} was made by running an absorption curve after the time for equilibrium had been reached. The range was the same as the one obtained for material at Rf = 0.65.

It should be noted that the chromatographic procedures described could be used for purification of lead tagged with Pb^{210} as well as for preparation of Bi^{210} and Po^{210} in a high state of purity. This is important when one desires to study the radioactive properties of one

element without interference of any radioactive impurity. In general, the principal methods for the isolation and purification of carrier-free tracers are (*13*): coprecipitation, ion-exchange adsorption, solvent extraction, and volatilization. To these paper chromatography could be added, especially in case the purpose of purification is to get the element free from other radioactive species, for study of its nuclear properties.

If the experiment is to be used for instructional purpose some macrochemical test could be made on the solution before the development of the chromatograms; it will be quite interesting to observe that although the test will show lead as the only cation present and bismuth was not detected, the chromatographic process will show that bismuth and polonium were also in the solution.

ACKNOWLEDGMENT

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HILMAR JOHANNES BACKER

H. S. VAN KLOOSTER
Rensselaer Polytechnic Institute, Troy, New York

Still engaged in research after his official retirement at the age of 70 in September, 1952, Hilmar Johannes Backer continues as acting head of the organic laboratory of the University of Groningen until the arrival of his successor, Arens, of the University of Bandoeng, Java.

Born on January 13, 1882, in Dordrecht, where he received his early education, Backer entered the University of Leyden in 1902 and took his doctorate on July 6, 1911, with a thesis suggested by his promoter, Franchimont, at that time the dean of organic chemists in Holland. After his promotion Backer continued his researches, partly in collaboration with Franchimont, and on May 22, 1913, he started his academic career as Privaat-docent with a public lecture on "Physical characteristics of organic compounds."

After two years of outside activity, first in the municipal testing laboratory of The Hague and later in the laboratory of the Treasury Department in Amsterdam, he was appointed to the chair of organic chemistry at the University of Groningen, one which had become vacant through the death of the incumbent, J. F. Eykman. Backer's vision of the future of organic chemistry was aptly expressed in his inaugural address: "The power and the ideals of organic chemistry." Backer's newly built organic laboratory was opened in December, 1917, with a historical essay, "Old chemical instruments and laboratories from Zosimos to Boerhave." His long and fruitful work in Groningen has covered a period of 37 years, during which more than 70 doctoral theses were completed by his students. About 40 of these dealt with the chemistry of organic sulfur compounds. The results obtained have been published in the *Recueil des travaux chimiques des Pays-Bas*, to which Backer has been an active contributor for nearly 40 years.

Backer played an important part in the official life of the University, and as Rector Magnificus he directed its affairs in the academic year 1930–31. He was an active member of the Dutch Chemical Society from its beginning. He seldom misses the annual meetings of the Society, which are held in July in one of the

principal cities of Holland, and his many friends always eagerly welcome him and his sister, who often accompanies him, since he has never married. Perhaps he, like Bunsen, "never found time to do so." He has, however, a large "family" composed of his pupils and former students, for whom he has been and is still, in many respects, more than a father. He has taken his students by bicycle, boat, or train on numerous excursions nearby and far away. In 1918 he established a student excursion club that organized study trips to Hanover, to the Harz mountains, to Czechoslovakia (in 1921), and to other countries. In 1951 at the seventy-fifth anniversary of the American Chemical Society, Backer managed to take five of his students along to participate in the meetings and trips organized for that occasion.

During the war years, when academic activities were largely suspended, Backer, at the risk of his life, helped students who had gone under cover. At the end of the occupation he was imprisoned for a short time and was ultimately set free by the advancing Canadian troops.

At the recent semicentennial of the Dutch Chemical Society Backer received an honorary membership. The special issue of *Chemisch Weekblad* published on that occasion contains Backer's review of Dutch chemistry in the past 50 years, work in which he has been an active contributor for over 40 years. With characteristic modesty he mentions his own work in footnotes while giving full credit to that of his students.

Well known outside his own country, Backer has lectured in Belgium, France, the United States, and elsewhere. He is a member of the Royal Academy of Sciences in Amsterdam and holds honorary degrees from the Universities of Ghent and Lille. His students have honored him on numerous occasions and their fervent hope is that he may be able to continue his fruitful work for years to come.

OTIS COE JOHNSON AND REDOX EQUATIONS

GEORGE W. BENNETT
Grove City College, Grove City, Pennsylvania

More than seventy years ago Otis Coe Johnson set forth his method for balancing oxidation-reduction equations.[1] Although Johnson himself was at pains to point out that he used the terms positive and negative in an arithmetic sense and not in terms of electrical polarity, others have attempted to superimpose electron concepts of valence onto the Johnson method. After a quarter of a century of such efforts chemists are about agreed that these newer concepts are "convenient fiction,"[2, 3] and that it should be admitted that conventional methods for balancing redox equations are empirical. But if the inquiring student wishes to know what real basis of fact underlies this very useful method, what shall he be told?

It is the purpose of this paper to point out what is basic verity and what is empiricism in Johnson's method of balancing redox equations. The verity is that the coefficients of a redox equation are dependent on the ratio of the redox equivalent proportions of the reactants. The empiricism in the method lies in the procedure for ascertaining the equivalent proportions. And in the background stands Johnson's concept of valence.

Redox reagents differ from simple reagents in respect to their equivalent weights; in the latter the equivalent weight is invariant, whereas in the former the equivalent weight is variable and depends on the reaction in question. Redox equations are difficult to balance because it is not readily apparent, in most cases, what the equivalent weight is for the given reaction. The problem, therefore, becomes one of ascertaining the reacting ratios of the chemicals involved.

If one is given the equivalent proportions of the reactants in a redox equation it is relatively easy to balance the equation by inspection. Thus if a redox equation is written in terms of equivalents, as for example,

$$\frac{a\mathrm{KMnO_4}}{5} + \frac{b\mathrm{H_2C_2O_4}}{2} + \frac{c\mathrm{H_2SO_4}}{2} = \frac{d\mathrm{MnSO_4}}{5} + \frac{e\mathrm{CO_2}}{1} + \frac{f\mathrm{K_2SO_4}}{2} + \frac{g\mathrm{H_2O}}{2}$$

It is readily balanceable by inspection although some of the coefficients emerge as unfamiliar fractions instead of the usual whole numbers. The fractions could be eliminated in this case by multiplying all terms first by

[1] Johnson, O. C., *Chem. News*, **42**, 51 (1880).
[2] Vander Werf, C. A., W. A. Davidson, and H. H. Sisler, J. Chem. Educ., **22**, 450–6 (1945).
[3] Vander Wer[illegible], C. A., *ibid.*, **25**, 547–51 (1948).

five and then by two. In so doing it becomes apparent why "the change in the oxidation number of the oxidizing agent becomes the coefficient of the reducing agent, and vice versa"; this step is simply an arithmetical operation to excise fractions. Most beginners, however, learn this operation only as a mysterious know-how and not as a know-why.

The beginner, of course, will not glibly set down equivalents. Three courses for determining such values are open to him. First he might, like his chemical forefathers, determine them experimentally, a laborious task in even one instance. Or he might be able to deduce them with the help of his instructor, given equations for a series of related reactions which lead eventually to oxygen or hydrogen as reference, provided he has learned well the definition of equivalent weight. But even the good student will hardly be able to produce related equations under his own power. A third way of deducing equivalent weights would be to utilize some good rule of thumb which might tell "what" without telling "why." Johnson devised such a rule.

The crux of the Johnson rule for determining chemical equivalents in redox reactions is that compounds are treated in the same manner as elements. Our chemical forefathers determined the combining capacities of elements from the ratio of their atomic weights to their experimentally determined combining weights, and this capacity they termed valence. Since free elements manifest no combining capacity they had, by this definition, zero valence. When, however, a free element combined with a second element or group of atoms, the combining weight referred to the atomic weight of the element indicated its valence. And, vice versa, where valence changes were known, equivalent weights could be deduced. Valence, to the founding fathers, was always positive; negative valence had no meaning. Johnson, of course, could not speak of the change in valence of a compound since by definition the term valence alluded to the bebavior of elements, but he could think of a change in the combining capacity of a compound. If a compound before reacting were treated in the same manner as a free element, that is, as manifesting a zero combining capacity, then its equivalent weight in a redox reaction could be deduced by the change in the ratio of its experimentally determined combining capacity and its molecular weight. And again, vice versa, where changes in combining capacity were known the equivalent weights of compounds could be deduced.

Thus in the reaction

$$2SO_2 + O_2 = 2SO_3$$

each molecule of SO_2 has reacted with two equivalents of oxygen, which is another way of saying that the combining capacity of SO_2 (as well as of the sulfur in it) has increased by two units in forming SO_3, hence the equivalent weight is $SO_2/_2$.

Instead of the terms valence, or combining capacity, Johnson coined the term "oxidation stage" for use with his new rule. And, although negative valence was not possible, a negative stage of oxidation (in an arithmetic sense) is conceivable. For example, we write

$$N_2 + O_2 = 2NO$$
$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

In the first case each atom of nitrogen requires two equivalents of oxygen to produce NO, but in the second case each molecule of ammonia requires five equivalents of oxygen to cause the nitrogen to reach the same stage of oxidation. Johnson ascribed to the nitrogen in ammonia, therefore, a negative stage of oxidation of three units, negative, that is, in an arithmetic sense. Or again, the oxidation stage has been altered by five units to reach a positive stage of two in NO.

One can determine these changes in degree of oxidation, and hence the equivalent weight, by the rule of thumb which Johnson invented. This rule is to ascribe to oxygen in compounds an oxidation stage of minus two and to hydrogen a stage of plus one, the remaining element or elements acquiring the necessary sign and values to make the compound as a whole have a zero oxidation stage. This scheme ascribes the entire change of oxidation stage in reactions to one or two elements in the compound instead of to the compound as a whole. Such a scheme is empirical; the equivalent weights are determined by rule of thumb and not by some obvious chemical relationship.

While Johnson himself had no thought of ascribing positive and negative bonds to particular atoms within a molecule, others have attempted to do so.[4] In so doing new terms appear: "formal charge," "relative valence," "polar number," "oxidation level," "oxidation state"; but in the end it amounts to the fiction of electron transfer where covalent bonds are involved. The efforts to relate Johnson's method to modern concepts of valence have given rise to the "convenient fiction" and have tended to obscure what was obvious seventy years ago, namely, that Johnson's method is rule of thumb.

If both teacher and student understand Johnson's concept of the relation between valence, atomic weight, combining weight, and oxidation stage, then it will be apparent that the verity in the Johnson method is that his rule does give the equivalent ratios for redox reactions. The empiricism lies in the procedure for ascertaining the equivalent ratios. The method is useful, not because it gives insight into the nature of valence changes, but because it is convenient and expeditious for determining the all-important coefficients of the oxidizer and the reducer.

[4] FERGUSON, L. N., J. CHEM. EDUC., **23**, 550–4 (1946).

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THE OBJECTIVES OF A COLLEGE COURSE IN INSTRUMENTAL ANALYSIS[1]

HOWARD A. STROBEL
Duke University, Durham, North Carolina

MEASUREMENTS have never been made in such variety or been so important in chemical pursuits as they are today. The industrial process line bespeaks this development with its continuous detection and recording devices and its automatic controls. It is even more apparent in the research laboratory where complex optical and electronic instruments of high sensitivity and reliability are in everyday use. In short, physical or instrumental approaches to the obtaining of data, to *analysis* and *control*, are proving themselves: they are increasingly satisfying our demand for methods of measurement which are more rapid and elegant, and often more reliable and sensitive, than the classic "chemical" techniques.

Aside from on-the-job or on-the-research-problem familiarization, instruction in these new instruments and procedures has been taken over largely by universities and colleges. At first it was incorporated into their regular analytical offerings. Since 1940 the number of techniques and devices clamoring for inclusion has been steadily increasing, however, and colleges have had to reconsider and reorganize their instruction in this field. We know that the general solution has been the establishment of a separate course in instrumental analysis. It is worth noting that this type of course marks a departure from the others available in chemistry, for in it, chemistry as such provides only applicative illustrations, and physical theory, techniques, and types of apparatus are emphasized. At least one of these courses has been described in some detail (*1*).

Not all colleges adopted the idea of a separate course. There are at least two publicized alternatives which have found favor: (*a*) the organization of a course in special topics in analysis which devotes a part of a semester to instrumental methods (*2*), and (*b*) the development of a course intended primarily to provide technical rather than fundamental training (*3*). The latter has appeal in regions where there are concentrations of chemical industry. Though each alternative, as well as others which have been devised, meets the need for instruction, both differ basically in outlook and in teaching objectives from what may be termed a "regular" course in instrumental analysis.

It is this matter of goals for a regular course that we may profitably analyze. There is probably little disagreement today over the main types of experimental material which should be a part of the subject. Rather the debatable question is that of objectives. Whether "regular" courses in the field should in any sense be intended for the training of technicians can surely be answered negatively. Logically, it seems that any adequate set of objectives has two interrelated aspects: (*a*) the characteristics sought in students completing the course, and (*b*) the relevance of particular approaches as a part of chemical training and the emphasis on each to be conveyed to the student.

With regard to the first aspect, an instrumental course may be described as intending to produce chemists with insight into, and some experience with, instrumentation. Broadly, it should turn out students who not only look beyond the particular to recognize general characteristics of the different methods with which they work, but who also can draw on their theoretical background with reasonable success for intelligent operation, adaptation, and if necessary, extension of present physical methods.

The aspect of relevance and emphasis, on the other hand, allows the handling of goals in more specific terms—it determines in the light of the first aspect the make-up of the course. One now asks what particular instruments and experiments will best demonstrate general principles without losing the student in operational details. And will the student's imagination be stimulated so that he will learn to ask relevant questions as well as perform the assigned project? Also, to what extent should the emphasis in lectures and discussion be on fundamentals of theory rather than on applications? A host of pertinent questions occur to us.

The answers to these, of course, are various. Particular research interests and industrial contacts at different universities are rightly reflected in the subject matter and slant of their instrumental analysis courses. Budget limitations often dictate the use of simple instruments wherever possible with provision for a gradual expansion of the experimental offerings as more equipment can be bought. Serfass (*4*) has skillfully discussed the problems of budgeting for such a course. Another factor contributing to differences between courses, one which influences decidedly the distribution of time between details and generalities, is the background required of students in the course.

These are healthy differences since diversity insures a reception for new ideas and is thus a source of strength. In the matter of the definition of the scope

[1] Based in part on a paper given before the Division of Analytical Chemistry, at the 123rd Meeting of the American Chemical Society, Los Angeles, March, 1953.

of this field, however, agreement is more important. There is no doubt that the broad aspects of instrumental methods, apart from any particular discipline—in our case, chemistry—should be stressed. Indeed, it appears that in generating a broad view all students gain in professional character, and the alert students are really challenged. There is also no doubt, unfortunately, that such generalities will be received without appreciation or perhaps even without comprehension by students with too scanty an acquaintance with certain branches of physics, mathematics, and chemistry. Some good methods of attacking this problem suggest themselves immediately. The establishment of adequate prerequisites is one, for it will tend to provide students with sufficient background. A second is class review of basic areas together with the introduction of necessary "new" material in fields the students seldom explore in a regular chemistry curriculum. A final step in preparing for generalization can be collateral reading preferably in conjunction with laboratory projects.

With the stage set, we may ask with interest whether the general aspects of a *chemical* course in instrumental analysis can be effectively presented within a conceptual framework such as that provided by the *science of instrumentation*. Much has been written and spoken in the last few years about the emergence of such a science (*5*, *6*). Admittedly, its identification with physics and engineering has been stronger than that with chemistry. Yet its province quite naturally includes our field. In fact, this infant science seems to furnish the integrating factor sought because it is inherently concerned with the operations involved in making measurements. This type of fundamental consideration can certainly help chemistry students to correlate their laboratory and lecture experience in instrumental analysis.

How and when should the concepts of the science of instrumentation be introduced for best effect? It appears to be a matter for individual decision. Logically, the process can begin in the instrumental course as basic optical and electronic principles are discussed. These are certainly the ideas most necessary for an understanding of measurement processes. One needs only to list the operations comprising a measurement to illustrate the point. They are: (*a*) *detection* or *sensing* of the quantity of importance, (*b*) *transducing* or *transforming* the basic stimulus into something which can be handled with facility, (*c*) *amplification* or *transmission* of the signal, and (*d*) *presentation* of the information (as a line on a chart, etc.). Optics is most often employed in the first step, as, *e. g.*, in spectrophotometry where the concentration of a component is sensed as an intensity of light of a certain wave length. In the remaining stages of a measurement, and sometimes in the first, electronics is clearly implied.

Again the science of instrumentation in its concern with the reproducibility and accuracy of measurements helps to systematize and emphasize the techniques for evaluating the validity of results. Usually the student requires a reintroduction and much strengthening in his ability to handle data, since his previous contact in quantitative analysis or physical chemistry is likely to have been shallow and unrevealing of the statistical basis of error considerations. The strengthening ought to take the form of a discussion of the normal error curve, precision indices, the propagation of errors, and the significance of least squares analysis. As time allows, the basis for a critical appraisal of the design of experiments and instruments may also be indicated.

INSTRUMENTAL ANALYSIS AT DUKE UNIVERSITY

The foregoing remarks have intentionally been quite general. In order to indicate how these ideas have been implemented in at least one instance, a specific instrumental analysis program, the one at Duke University, will be described. As that program evolved, under Professors W. C. Vosburgh, M. E. Hobbs, and the author, the following general aims were kept in mind.

(1) The course work should supplement the regular physical chemistry and advanced quantitative analysis courses (implying basically a reconsideration of the laboratory experiments in physical chemistry) and should give students a working familiarity with representative optical, electronic, and mechanical instruments.

(2) The instructional approach should be as fundamental as seemed feasible and should allow the student to acquire a critical appreciation of the relative advantages and limitations of various instrumental techniques.

To meet these aims two one-semester courses have been formulated. It is intended that the student secure a broad introduction to instrumental techniques whether he is able to complete one or both courses, though one course concentrates on optical approaches and the other on electronic and a few other physico-chemical fields. Both are offered on the senior-graduate level. All B.S. and most B.A. chemistry majors and all the incoming graduate students who have not had similar training elsewhere take at least one semester of instrumental analysis.

The structure of the courses emphasizes the central place of experimental work. Each week one hour is devoted to lecture and three hours to the laboratory. Both the lectures and the collateral reading assigned (in a variety of source books) are intended in a real sense as background for the laboratory projects. A sufficient variety of experiments is available so that individual interests can be recognized, and any duplication is avoided for the two-semester student. A listing of the apparatus used is given in Tables 1 and 2.

Lectures. Lecture and discussion time is given over to developing a qualitative grasp of pertinent optical, electronic, and physico-chemical principles. Operational details of equipment are seldom discussed in class, although certain standard components such as dispersing prisms and photoelectric cells are considered at length. Some time is also given to experimental

procedures, since they focus attention on the measurement processes and define the result to be obtained from the determinations.

Each course begins with a discussion of error analysis. In presenting the statistical background for the calculation of means and precision measures and for making a least-squares analysis or a study of error propagation ample experimental illustrations are brought in. Means of selecting reliable experimental procedures are also considered. These statistical concepts are employed by the student later in the laboratory in discussions of data and equipment in reports.

The concentration on optics in the first course acquaints the student qualitatively with the nature of and the basis for (1) emission and absorption spectra; (2) refraction, absorption, reflection, polarization, and scattering of light; and (3) typical optical apparatus.

After duplicating the first semester's coverage of error analysis and spectroscopy, lectures in the second course are devoted to selected topics in (1) electronics, (2) electrochemistry and polarography, (3) fractional distillation theory, and (4) typical electronic apparatus.

Laboratory Projects. As long as there seems to be no serious loss of operating efficiency, a research-oriented point of view is taken in the laboratory. Project goals are often stated broadly. Detailed procedures by which they may be realized are not always specified but are left to the student's discretion. In this connection much is required of the laboratory instructors; they are expected to make helpful and cogent suggestions about techniques, particular data which must be secured, and simple checks for proper operation of instruments. The pamphlets supplied by the instrument manufacturers are available to the student and serve as the principal source of information about the construction and operation of the instruments, as is true for a person doing research.

Whenever feasible, equipment lending itself to "exploration" by the student is provided for the projects. Ideally a happy compromise is sought between (1) the apparent simplicity of advanced commercial designs where all components except indicating dials and control knobs are neatly concealed within a "black box," and (2) the confusing complexity of strictly home-made equipment with its array of individual components. There are many makes of commercial apparatus of rather open construction which can be effectively used. An example of such a selection is the Cenco-Sheard Photelometer for absorption photometry. Even with the more compact types, it is expected that the students will examine all readily accessible features. The introduction to electronics, on the other hand, is done with the aid of student-constructed bread-board setups of a vacuum-tube voltmeter, a rectified power supply, and a phototube detector. These "exploded" layouts allow the display of components and a study of circuit diagrams, and make the results of adjusting circuit variables clearer. Also, where an assembling of components is necessary for a particular experiment, the student is responsible in most cases for carrying it out after discussing the steps he believes will accomplish the sought goal. This approach, we believe, results in a "feeling" and understanding of the operation of equipment which is not gained if compact, commercial pieces of apparatus are the only types handled.

TABLE 1
Optical Instruments Employed in Projects

Simple prism spectroscope	Spectrograph (visual and near ultraviolet)
Photoelectric filter photometer	Refractometers
Spectrophotometer (visual)	Polarimeter
Flame photometer	Compound microscope (three projects)
Fluorophotometer	Polarizing microscope (two projects)

OBJECTIVES

In concluding, the statements of Bassett, *et al.* (*1*) must be seconded: it seems incontestable that instrumental methods courses should be laboratory courses even though a limitation on the number of students who can be handled and the number of projects available is necessary. In the latter instance the experimental offerings may be expanded from year to year as new items of equipment can be purchased or constructed. Often it is found possible to have available for such a course portable equipment not in constant use for research.

In the matter of objectives it may be argued that the place of generalization has been too much stressed, that most students are unprepared even at the senior-graduate level for the heady dose suggested. Perhaps too much is being presumed of the student's ability to think precisely and to analyze. At least to some degree, however, those faculties should already have been developed when the student enrolls, and further growth ought to occur in the instrumental course. The point is that the small fraction of course time which can be given over to an introduction to general principles, to the science of instrumentation, if you like, should make a real contribution to the professional character of the student turned out.

TABLE 2
Electric and Electronic Equipment Used in Instrumental Projects

"Breadboard" vacuum-tube voltmeter, phototube detector, and power supply
Conductance bridge (conductometric titration)
Micromax recorder (fractional distillation)
Mueller resistance bridge (thermometer calibration)
Oscillator, heterodyne beat (dipole moment determination)
Potentiometer, type K (e. m. f. of cells)
Polarograph
pH meter (dissociation constants determination)
Scaler (distribution coefficient determination)

The instrumental analysis courses are liked by students; they give the definite impression of bridging many scientific fields and of translating theory into practice. It is hoped that they also leave the student with some of the broad ideas mentioned. The most valuable of these is undoubtedly the realization that the key to physical methods of measurement or analysis is in finding properties of substances which can be measured. With the theoretical background and experience in handling representative types of equipment, the student should feel some confidence in selecting a good instrumental method for a particular analysis.

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TEXTBOOK ERRORS AND THE SCIENTIFIC ATTITUDE[1]

WILLIAM E. MORRELL
University of Illinois, Urbana, Illinois

Every textbook contains errors. An attempt has been made to put them to profitable use.

The fostering of a scientific attitude in students is one of the objectives of practically every science course. An alert skepticism, a refusal to accept statements without evidence, a confidence in one's own objective judgment—these are some of the aspects of a scientific attitude. The usual unquestioning acceptance of anything seen in print is the antithesis of a scientific attitude.

In an attempt to encourage a critical spirit in students, and to encourage careful observation and thorough study, an experiment was tried in which students were given a grade-point bonus for each error they found in the textbook. In each discussion section the bonus for any particular error was given to the first student in the section who called his instructor's attention to the mistake. (Writing the student's name and section number by the side of the error at the time it was reported proved to be the easiest way to keep priorities straight.) By giving the bonus to the first student who reported the error it was hoped that prompt study of the text (instead of last-minute cramming) would be another outcome of the project.

The errors were reported orally between classes or on slips of paper handed to the instructor, so no class time was taken for the exercise.

The bonus in each discussion section for each error was three points on a scale in which each hour-examination was graded on the basis of 100 points, and 550 points represented a perfect score for the course, without the bonuses. In other words, each error for which a student received credit would add somewhat more than 0.5 per cent to his total grade.

The text which was being used, while fundamentally sound, had more than its share of minor mistakes. (The science textbook that contained no errors would be a rare one indeed.) These were of various kinds. Some were typographical ("Na_2Co_3," carbon shown with five bonds, C_6H_{14} called "hexene," etc.). Some were errors in grammar. Some were contradictions. Some were statements like "...as was shown on page 100," when page 100 contained no reference whatever to the matter; or "*Cf.* Fig. 50," when Figure 51 was meant. Some were errors of fact. Some were references to earlier definitions which turned out to be non-existent in the book. Some of the mistakes were obvious; others were more subtle and would be uncovered only through careful study.

Thirty-three was the largest number of different errors accumulated during the semester by a single discussion section, with 25 being the average accumulated by each section of 12–13 students. The largest number for which a single student received credit was 20. (She already had an "A.")

As might have been expected, the better students were more successful in finding mistakes than were the poorer ones. The "A" students received the bonus

[1] Presented before the Division of Chemical Education of the American Chemical Society, Chicago, September, 1953.

nearly five times apiece (on the average), while many of the poorer students didn't find a single error. Details are summarized in Tables 1 and 2.

STUDENT EVALUATIONS

At the end of the semester the students were asked to express their opinions and evaluations of the "experiment." They answered a questionnaire without signing their names, though they were asked to indicate the approximate number of errors for which they had received bonuses, by checking one of the following: 0, 1–2, 3–5, 6 or more.

The opinions varied from statements that the exercise had been of considerable value to expressions of disdain and resentment. A summary of the questions and replies follows.

"What effect—if any—did the bonus given for finding errors in the textbook have on the manner and effectiveness with which you studied the text?"

Of the 107 respondents, six reported undesirable effects (such as "wrong emphasis in study"), 56 reported "no effect," 33 listed benefits ("read more carefully, critically," etc.), and the remaining 12 misinterpreted the question, or gave answers which couldn't be classified, or gave no answer. In other words, of those (6 + 56 + 33) who gave a clear-cut answer, 35 per cent reported increased effectiveness in their study of the text, owing to the watch for errors.

There was a definite correlation between the number of errors found and the expressed improvement in effectiveness of study. Of those who reported no errors, 17 per cent of the clear-cut answers indicated increased effectiveness of study; of those given bonuses for 1–2 errors, 33 per cent reported increased effectiveness; 3–5 errors, 59 per cent; 6 or more, 75 per cent.

TABLE 1

Final grade	*Number of grades assigned*	*No. of these who received at least one bonus*	*No. of these raised from lower letter by bonus*	*No. of errors credited*	*Average no. of errors credited per student*
A	15	11	4	73	4.9
B	31	18	10	83	2.7
C	59	20	1	63	1.1
D	5	1	0	1	0.2
Failure	2	0	..	0	0.0
Totals	112	50	15	220[a]	2.0

[a] *Note:* These were not 220 *different* errors. There were many duplications, because a single error could have been reported and credited in each of the nine discussion sections.

"What effect—if any—did the bonus given for finding errors in the textbook have on the amount of time you spent studying the text?"

Of the 107 respondents, 61 reported "no effect," 29 reported studying longer (from a little extra to a great deal), and 17 misinterpreted the question, or gave an answer which chouldn't be classified, or gave no answer. Of those (61 + 29) who gave a clear-cut answer, 32 per cent reported more time spent studying the text than would otherwise have been spent. Again, and not unexpectedly, there was a definite correlation between number of errors credited and extra time spent studying the text. This is shown in the following series, in which the number of errors credited per student is followed by the per cent of respondents who indicated a desirable effect: 0 errors credited, 13 per cent favorable; 1–2, 32 per cent; 3–5, 60 per cent; 6 or more, 80 per cent.

TABLE 2

No. of errors credited to individual	*No. of students of each grade who received credit for the number of errors listed at the left*				
	A	B	C	D	Failure
0	4	13	39	4	2
1	1	5	5	1	..
2	2	3	4	..	..
3	1	2	4	..	..
4	2	..	1	..	..
5	1	..	3	..	..
6	..	2	2	..	..
7	..	3	1	..	..
8	..	1	..	..	..
9	1	..	..	..	..
10	..	..	..	..	..
11	1	..	..	..	..
12	1	1	..	..	..
13	..	1	..	..	..
20	1	..	..	..	..

"What effect—if any—did the bonus given for finding errors in the textbook have on the time (earliness) at which you studied the text?"

Twenty-two of the 94 clear-cut answers, or 23 per cent, reported studying more promptly. Broken down as before, the replies were as follows: 0 errors credited, 8 per cent favorable; 1–2, 47 per cent; 3–5, 24 per cent; 6 or more, 50 per cent.

"What effect—if any—has this watching for errors had on your attitude toward the textbook?"

Answers such as "more critical," "now realize books aren't infallible," were judged as showing desirable outcomes, and were found in the following percentages of clear-cut cases: 0 errors credited, 29 per cent; 1–2, 72 per cent; 3–5, 62 per cent; 6 or more, 78 per cent.

"What effect—if any—has it had on your attitude toward other textbooks and printed matter in general?"

As in the previous cases, "no effect" was a frequent answer, but replies such as "more skeptical" and similar desirable attitudes were expressed in the following percentages of cases: 0 errors credited, 28 per cent; 1–2, 60 per cent; 3–5, 75 per cent; 6 or more, 82 per cent.

"Was this bonus-giving plan a good idea or not? Were the net results beneficial or harmful?"

Forty-five replies (from "of doubtful value" to "lousy") were considered unfavorable, while an equal number (of corresponding range) were classed as favorable. The remainder were neutral or fence-straddlers. The definite trend found in previous cases appeared again: 0 errors credited, 33 per cent favorable; 1–2, 47 per cent; 3–5, 67 per cent; 6 or more, 82 per cent.

Report of the NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

OFFICIAL BUSINESS

272nd MEETING

The 272nd meeting of the NEACT was held at Spaulding High School, Rochester, New Hampshire, on October 10, 1953. The fall meeting that is held in the Northern Division of the NEACT is always characterized by a view of autumn foliage. This meeting was no exception and permitted the members to visit the outstanding plant of the Spaulding High School under very favorable circumstances. Paul R. Doe, of the faculty of the host school, assisted the division chairman in making those arrangements that make a meeting go smoothly.

First on the program was Austin S. Kibbee, Jr., of Lewiston High School, Lewiston, Maine, who spoke on "House-building—a summer course in science." He described some of the operations he had experienced which are better understood and better supervised when scientific principles are recognized and adhered to. His experiences with a water douser were illuminating!

Richard D. Wells, Research Director of the Bates Manufacturing Company, spoke on "Research." He lucidly pictured the purposes and motivations which guide research, with particular emphasis on subjective ones such as desire for personal recognition, impatience with existing methods, and desire for material gain. Much research has been done also with the motive of revenge or spite. Aspects such as these which are not ordinarily pointed out gave his talk exceptional value.

After the luncheon, Richard L. Demmerle of the General Aniline and Film Corporation spoke on the need for broadening the education of today's science students. He gave several excellent illustrations, taken from his experience, of instances in which young scientists needed to draw on resources other than their purely scientific background. Particular emphasis was laid on the understanding of the relationship between personality and type of job.

At the brief business meeting, the following new members were welcomed into the Association:

James Collins, S. J., Boston College High School, Boston, Mass.
John O. Edwards, Assistant Professor of Chemistry, Brown University, Providence, Rhode Island.
Saul Geffner, Chairman of Science Department, Far Rockaway High School, Far Rockaway, New York.
Henry A. Kuligowski, Science Teacher, Bacon Academy, Colchester, Connecticut.
George B. Moulton, Instructor, New Hampton School for Boys, New Hampton, New Hampshire.

President Dorothy W. Gifford read a letter from John E. Cavelti, Allegheny College, now at University of Hawaii, in which he acknowledged felicitations on the success of the Fifteenth Summer Conference. She also referred to a letter from Professor Fletcher Watson of Harvard, who reports that it is now possible to procure microcurie quantities of radioisotopes from the Deaconess Hospital in Boston for secondary-school and college use.

A vote of thanks was extended to the Spaulding High School for its hospitality.

273rd MEETING

The 273rd meeting of the NEACT, held jointly with the New England Biological Association and the Eastern Association of Physics Teachers, convened at Brandeis University, Waltham, Massachusetts, on December 5, 1953. The weather was propitious and an estimated 100 members from the three Associations attended. The University was a very cordial host and provided an excellent noon-day meal. To one making a first visit to the campus, the whole physical plant and the rapid progress made in six years of operation were an eye opener.

President Abram L. Sachar gave the welcoming address and emphasized the fact that Brandeis University represents the first corporate contribution of the Jewish community toward American public education. He also announced the accreditation of the University by the New England Association of College and Secondary Schools, given the day before, and the receipt of a handsome grant from the Hayden Foundation to be used in the future toward a new science building.

Saul G. Cohen, Chairman of the School of Science at Brandeis, followed with a short address on the science program being developed at the University, one aimed toward interrelating and telescoping the whole science program. He mentioned briefly the inauguration of graduate work in chemistry, to be followed soon by physics and biology.

Ralph L. Mondano of the Raytheon Manufacturing Company, Waltham, Massachusetts, was the third speaker of the morning and gave a technical discussion of the use of plastics in the electronic industry. An interesting development mentioned by Mr. Mondano concerned the irradiation of a plastic material, thereby

driving hydrogen out of the polyethylene carbon chain and giving rise to a double-bonded cross linkage.

O. J. Whittemore of the Norton Company, Worcester, Massachusetts, was the final morning speaker. His talk embraced a description of some of the research work with which his company is currently engaged, on the continuing search for new high-temperature refractories, their preparation, properties, and uses. He directed a portion of his talk toward the need for vocational guidance of young people into the ceramics industry, nowadays a very large field with many and varied opportunities and not overcrowded.

Elkan R. Blout of the Polaroid Corporation, Cambridge, Massachusetts, was the afternoon speaker and described a new instrument, the color-translating ultraviolet microscope, which is a combination of a microscope, a camera using ultraviolet light, and a processing unit which renders a microphotograph of, for example, a biological specimen in colors of the visible spectrum. Compared with the ordinary staining technique, the colored photographs that result from this process show greater resolution and definition. The colors, on the other hand, are not necessarily the same as those of the specimen. Dr. Blout has been employed in the development of this instrument. From the photographs shown one may judge that the equipment is beyond the budgetary limits of all but the best endowed research laboratories.

Each of the three participating organizations held separate business sessions. The following new members were welcomed into NEACT:

H. Russell Beatty, President, Wentworth Institute, Boston, Massachusetts.
Everett W. Bennett, Research Chemist, Linde Air Products, Tonawanda, New York.
John Domijan, Science Teacher, Barnard School, New Britain, Connecticut.
Ralph C. Haist, Chemistry Master, Humberside Collegiate Institute, Toronto, Ontario, Canada.
Arno Heyn, Assistant Professor, Boston University, Boston, Massachusetts.
Donald B. Peck, Science Teacher, Litchfield High School, Litchfield, Connecticut.
Sister Simon Peter, O. P., St. Mary's High School, New Haven, Connecticut.
B. R. Stanerson, Assistant to the Executive Secretary, American Chemical Society, Washington, D. C.
Stephen S. Winter, Assistant Professor, Northeastern University, Boston, Massachusetts.

Summer Conference Committee. President Dorothy W. Gifford announced the appointment of the following committee for the Sixteenth Summer Conference to be held next August at the University of Massachusetts:

Chairman: Robert D. Eddy, Tufts College, Medford, Massachusetts.
Program Chairman: Edward L. Haenisch, Wabash College, Crawfordsville, Indiana.
Registrar-Treasurer: Alice Howe, Concord High School, Passumpsic, Vermont.
Representative of Host Institution: Walter S. Ritchie, University of Massachusetts, Amherst, Massachusetts.

Ex Officio:

Dorothy W. Gifford, Lincoln School, Providence, Rhode Island, President, NEACT.
Guy F. Burrill, Keene High School, Keene, New Hampshire, Co-chairman, 1953 Conference.
John E. Cavelti, Allegheny College, Meadville, Pennsylvania, Co-chairman, 1953 Conference.
William O. Brooks, Technical High School, Springfield, Massachusetts, Secretary, 1953 Conference.
Katherine M. Murphy, Dorchester High School for Girls, Dorchester, Massachusetts, Registrar-Treasurer, 1953 Conference.

Nelson J. Anderson, Suffolk University, Boston, Massachusetts.
Paul F. Davis, Bellows Falls High School, Bellows Falls, Vermont.
Paul R. Doe, Spaulding High School, Rochester, New Hampshire.
Richard W. Fessenden, University of Massachusetts, Amherst, Massachusetts.
Irwin H. Gawley, Jr., Tenafly High School, Tenafly, New Jersey.
Helen G. Hirst, Waltham High School, Waltham, Massachusetts.
Walter W. Holt, Boston University, Boston, Massachusetts.
Marguerite J. Houlihan, Lincoln Junior High School, Medford, Massachusetts.
Earl N. Johnston, Williston Academy, Easthampton, Massachusetts.
Bernard Jurale, Meriden High School, Meriden, Connecticut.
W. James Kilgour, Avon Old Farms, Avon, Connecticut.
Francis M. Lamoureux, Palmer High School, Palmer, Massachusetts.
Eldin V. Lynn, Massachusetts College of Pharmacy, Boston, Massachusetts.
Douglas G. Nicholson, East Tennessee State College, Johnson City, Tennessee.
Robert F. O'Malley, Boston College, Chestnut Hill, Massachusetts.
Helen G. Pratt, Lynn, Massachusetts.
Peter Richardson, Pomfret School, Pomfret, Connecticut.
Clarence D. L. Ropp, University of Bridgeport, Bridgeport, Connecticut.
Ida B. Routh, Bryant High School, Long Island City, New York.
John W. Sease, Wesleyan University, Middletown, Connecticut.
Fred G. Sowers, Torrington High School, Torrington, Connecticut.
Louise O. C. Swenson, English High School, Lynn, Massachusetts.
Angela M. Trovato, Beaton House, Exeter, New Hampshire.
Charles E. Walkden, Barrington High School, Barrington, Rhode Island.

John A. Timm, Simmons College, spoke about the proposal the Northeastern Section of the American Chemical Society is considering, of sponsoring a program of four to six lectures for secondary-school teachers in the Spring of 1954, in the Boston area, on a specific field of chemistry.

A vote of thanks to Brandeis University for its hospitality was taken.

LEALLYN B. CLAPP
Secretary

NECROLOGY

With regret the Necrology Committee reports the death of Irene E. Kenney of the Somerville High School, Somerville, Massachusetts, a member of NEACT since 1930.

S. WALTER HOYT
Chairman, Necrology Committee

● A BRIEF INTRODUCTION TO ORGANIC CHEMISTRY

Leland A. Underkofler, Professor of Chemistry, Iowa State College. D. Van Nostrand Co., Inc., New York, 1953. vii + 352 pp. 29 tables. 15 × 23 cm. $4.25.

THIS book is admirably suited to its purpose. Designed for the so-called short course in organic chemistry, it shows a nice balance between the undernourished outline and the overstuffed compendium, both of which have been offered for the terminal course.

In the present work an interesting innovation is the author's treatment of the order of presentation of the simpler organic types. After a preliminary chapter dealing with fundamental concepts the author gives an ordinary discussion of the saturated hydrocarbons. This is followed by the alcohols. The next two chapters are written so that they may be taught in either order. They cover, as written, the unsaturated hydrocarbons and the halogen derivatives of the hydrocarbons. Many teachers have taught these two topics in the order given but many undoubtedly prefer the reverse order. The order of presentation of the remaining types is more or less standard from here on. The carboxylic acids are discussed just before the aldehydes and ketones. The acid derivatives follow. The separation of the acids from their derivatives, a not uncommon practice, seems to this reviewer unnecessary and possibly confusing to the student.

Like all teachers of the short course in organic chemistry, Dr. Underkofler is confronted with the problem of how to treat the aromatic compounds. The answer in this case is to separate the aromatics from the aliphatics but a compromise is effected by presenting a discussion of aromatic hydrocarbons and their derivatives in seven pages at the end of the chapter on unsaturated aliphatic hydrocarbons. The section is written so that it may be used or not depending on whether time permits the more detailed discussion of aromatic compounds presented later in the book.

The type reactions are numbered as they occur in the text and are later collected in an appendix. This permits convenient reference to a list of typical reactions when needed for the solution of "to-from" exercises in organic syntheses.

A criticism of the book, and one which is by no means peculiar to the present work, is the introduction of types of compounds which are not treated until later in the book. This must be a most disturbing element so far as the student is concerned. Thus in the present instance the reactions given in what must be a very early lecture in the course for the preparation of the alkanes are: reduction of chloroform by zinc in ethyl alcohol; the action of sodium on alkyl halides; the action of water on the Grignard reagent; the action of heat on mixtures of sodium hydroxide and sodium salts of organic acids. One wonders what conception a beginning student has at this time of ethyl alcohol as a source of nascent hydrogen, of alkyl halides, of organometallic compounds, and of even the simpler aspects of organic acids. It might be a nice exercise to determine if a book on organic chemistry might be written which would avoid this practice entirely; or if such is not possible, just how few such instances need be invoked.

LIONEL JOSEPH

SAN DIEGO STATE COLLEGE
SAN DIEGO, CALIFORNIA

● MODERN RADIOCHEMICAL PRACTICE

G. B. Cook, Atomic Energy Research Establishment, Harwell, England, and *J. F. Duncan.* Oxford University Press, London, 1952. xx + 407 pp. Illustrated. 15 × 23.5 cm. $8.50.

THE meteoric rise in the usage of radioactive isotopes in research laboratories has necessitated the introduction of courses in nuclear chemical techniques in most universities and colleges. Cook and Duncan have produced a text admirably suited for a laboratory course for prospective utilizers of unstable isotopes.

The book covers the use of radioelements in chemical investigations, radiochemical separations, the properties and measurement of nuclear radiation, the production of isotopes, measurement errors, health physics, and an extensive set of suggested experiments.

The laboratory procedures seem to have been chosen with a great deal of care and provide experiments with a diversity of nuclides. However, many of the experiments require specific short-lived substances available to those only in close proximity to a pile. The experiments are described in a thorough and readily understandable manner.

Nuclear-measurement devices receive an excellent review, although the present writer wonders why so little space is devoted to the windowless flow counters which at present receive a great deal of use in this country. The discussion of sample preparation and absolute beta counting is excellent.

Although the book does not have enough detail for the advanced research worker, it fills the need for an experimental text in radiochemistry. There are relatively few errors and the large type is a delight. The use of English terminology (paralysis time, castle, etc.) will be diverting to most American readers.

EDWARD D. GOLDBERG

SCRIPPS INSTITUTION
LA JOLLA, CALIFORNIA

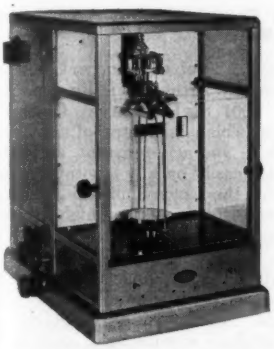
Out of the Editor's Basket

ew Analytical Balance

E. Machlett & Son has announced a new, ngle pan analytical balance to the labo- tory and scientific world. Named the mson Model S-M Balance, this new ient fic instrument was created and pro- uced by Wilhelm Spoerhase Co. of estern Germany—a firm with 121 years f experience in the manufacture and de- gn of analytical balances.

According to a Machlett spokesman, he chief advanatage of the Model S-M alance is that it minimizes operator fa- gue and still gives great speed, simplic- y, reproducibility, and dependability. his is achieved by the location of the asily manipulated, weight control knobs nd the vernier-type reading scale.

Numbered for rapid identification, the eight control knobs are located at the ower left side of the instrument to permit he operator to rest his elbows on the table hile selecting weights. The reading cale is located at eye level just above the eighing pan. As an added convenience o the operator, the instrument incorpo- ates two beam arresting knobs—one on ither side to permit arresting the beam ith left or right hand.



Machlett describes the construction of he apparatus as being "painstakingly recise." For example, its cantilever- ype beam—with a 10:1 ratio—is made of non-magnetic aluminum alloy. All bear- ng surfaces of the new Model S-M Bal- nce are made of knife edged, optically round sapphire to minimize frictional rror and provide durability. To give he lowest center of gravity and reduce ibration, all weights are located in the nstrument's completely enclosed base. Unimpaired visibility is assured by the all lass front and sides enclosing the working rea. While closed the interior is com- letely sealed eliminating the erratic ef- ects produced by body radiation, human reath, or outside drafts.

According to Machlett, extensive tests ith the Emson Model S-M Balance have shown actual weighing times to average less than 18 seconds. This speed is accomplished in part by the instrument's rapid-acting air-dampening device.

Complete details on the new Model S-M Balance are available from E. Machlett & Son, 220 E. 23rd St., N. Y.

A Contest for Teachers

"Why I Teach," a contest for teachers, to encourage good teachers to remain in the teaching profession and eligible young people to enter it, is again being sponsored by the American Legion Auxiliary. The contest opened November 1, 1953, and closes at midnight, May 1, 1954. Contestants must have completed five years of teaching by June 1, 1954, and each entry must be accompanied by a signed statement of release, giving the American Legion Auxiliary permission to use the entry.

Subject of this year's contest is "The purposes and goals of a teacher in a free America." The form of the essay must be an open letter to a high school graduate, and the entry must be between 100 and 300 words long.

Both Divisional and National awards will be given. The Divisional awards will consist of a $50 U. S. savings bond, to be given to the contestant having the winning entry in each of the five Divisions.

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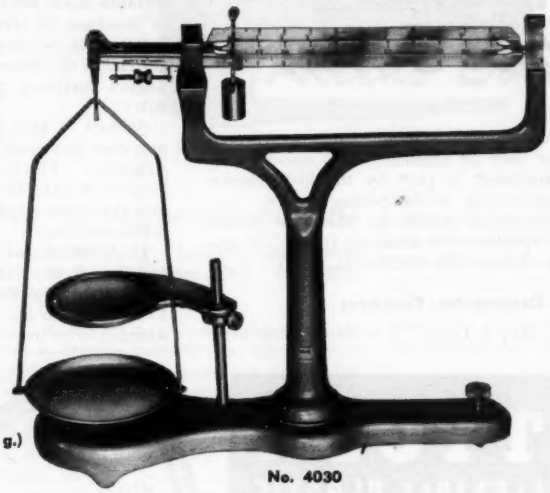

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The National award will consist of a $250 U. S. savings bond, and will go to one of the five Divisional winning contestants. In addition, each Department may give a Department award if it so desires.

Predictability Flowmeters

Complete predictability of all fluids has now been made by the Emil Greiner Co., 20–26 N. Moore St., New York 13, New York, with the development of their line of Predictability Flow meters.

Heretofore individual calibrations for each specific fluid were necessary. With Predictability Flowmeters the calibration curve can be calculated directly, without the experimental calibration that was necessary in the past. The only information required to obtain a calibration for a given fluid is the density and viscosity of the fluid under conditions of flow.

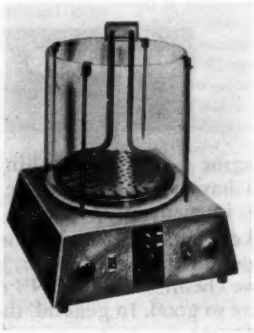
An important feature of these flowmeters is a new teflon stop which provides quick interchangeability and ball replacement at no extra cost.

A bulletin describing the Predictability Flowmeters is available from the Emil Greiner Co.

Magni-Whirl Jar Bath

A new jar bath with unusual features has just been announced by Blue M Electric Company. According to the manufacturer, the Magni-Whirl jar bath obsoletes the need for any motors, stirrers, or circulating systems of any type, yet provides complete uniformity and automatic, gentle, efficient agitation in all areas of bath irrespective of work load.

Complete uniformity and agitation is maintained by means of gentle pulsation of the Magni-Whirl perforated agitator plate. Plate is pulsated by a powerful electro magnet, located in base support. Actuation of magnet is accomplished by means of selenium rectifier, capacitor, and timed relay having long-life cadmium contacts.



Another outstanding feature is the automatic dual microtrol which permits automatic selection of any two most used temperatures within range of bath.

Detailed information may be had by writing the manufacturer, Blue M Electric Co., 306–08 West 69th St., Chicago 21, Illinois.

Pocket-size pH Meter

A new pocket-size pH meter giving instant, continuous, direct reading of pH with no buttons to hold down or dials to turn has been announced by Analytical Measurements, Inc., 585 Main Street, Chatham, New Jersey. It needs no supports, holders, beakers, or separate electrodes, and is completely self-contained in a waterproof case with a shoulder strap. Information may be obtained from the manufacturer.

Controlled Atmosphere Hood

A low cost and lightweight portable Controlled Atmosphere Hood is now being manufactured and distributed by the P. M. Lennard Co., Inc., 671 Bergen St., Brooklyn, New York. Heretofore, similar self-contained contamination control units have been custom-made for each job.

The Controlled Atmosphere Hood (C. A. Hood), constructed of a fiber-glass plastic material, creates a completely dry, sterile, inert, and dust-free atmosphere.

A unique and simple filter system with vacuum or pump allows the operator to select purification trains to control dust, bacteria, and moisture either individually or together. When necessary, hands or objects may be put in and removed freely without loss of internal pressures or control conditions.

The C. A. Hood is especially useful in the radioactive field because alpha and beta particles of higher energies and gamma photons of lower energies can be safely handled and completely controlled. Any required thickness of lead sheeting can be inserted between the laminated layers to provide the necessary radiation shield against gamma photons of energies higher than 100 millicuries.

Additional details are available from the manufacturer.

New, Chemical- and Acid-Resistant Sink Unit

A new, all-polyethylene sink unit is announced by Arthur S. LaPine and Company, 6001 S. Knox Ave., Chicago 29, Illinois, which is dentproof, breakproof, chemical- and acid-resistant, and may be installed easily on any laboratory sink.

Called the Lanco Sink Unit, this equipment consists of: stopper, high level drain, strainer, lock-nut, plug, trap, and outlet union.

Particular attention is called to the trap which may be unscrewed without the aid of tools. A few turns of this polyethylene trap produce a watertight joint without the need for washers.

Westinghouse Fellowships for Secondary School Teachers

Thirty fellowships, each valued at $250, will be awarded to secondary school science teachers who will participate in a special six weeks' summer program at Carnegie Institute of Technology, it was announced recently. The 1954 fellowships have been made available by the Westinghouse Educational Foundation. This marks the fourth annual program for the secondary school teachers of science.

The program of study stresses the importance of fundamental concepts in Chemistry, Physics and Mathematics and provides a survey of recent developments in the pure and applied sciences.

Throughout the program, emphasis is placed on teaching methods in which the Carnegie Plan of Professional Education is featured. The academic program consists of lectures on such topics as radioactivity, nuclear research, synthetic rubber, petroleum, and applied mathematics.

This program is supplemented by visits to Carnegie Tech's research and teaching laboratories and to some of the many great industrial establishments of the Pittsburgh area.

Eighteen units (six hours) of college credit will be granted for the academic work of this six-week program. Full-time staff members of the College of Engineering and Science will have charge of the course.

The program, which begins June 28 will extend through Friday, August 6, and no Saturday sessions will be held. A tuition fee of $50 will be charged for the six-week course and the balance of the $200 provided by the fellowships can be applied to commuting or living expenses.

Living accommodations in Carnegie dormitories will be available at reasonable rates. Dining facilities are accessible on the campus and, in addition, the School's recreational facilities will be available without charge to fellowship winners.

Application forms and further information about the summer program can be obtained from the Director of Summer Sessions, Carnegie Institute of Technology, Pittsburgh 13, Pa.

Enrollments Now Accepted for Oak Ridge School of Reactor Technology

The Oak Ridge School of Reactor Technology is now accepting applications for the 1954–55 session, according to an announcement by Dr. Fred C. Vonder-Lage, Director of the School. Applications for the class beginning in September must be submitted for review by the Committee on Admissions not later than March 15, 1954.

Approximately 80 students will be selected by the Atomic Energy Commission's Admissions Committee. Students eligible for the 50-week graduate course must hold a bachelor's degree or higher in chemistry, engineering, metallurgy, physics, or engineering-physics. The School is a part of Oak Ridge National Laboratory which is operated by Union Carbide and Carbon Corp. for the Atomic Energy Commission. It is one of the largest laboratories in the world, and is concerned with research and development in nearly all phases of nuclear science and technology.

Many of the leading industries, seeing the possibilities for peacetime application of reactor technology, are sponsoring students. Forty-eight members of the present class are sponsored students who remain on the payroll of their respective companies during the training period. The remaining members of the class, recent college graduates, are paid a monthly salary by Union Carbide and Carbon Corp. ORSORT has no tuition charge for the 50-week training session.

The curriculum will include such subjects as the following, as they apply to reactors: analysis and mathematics, chemistry and chemical technology, engineer-

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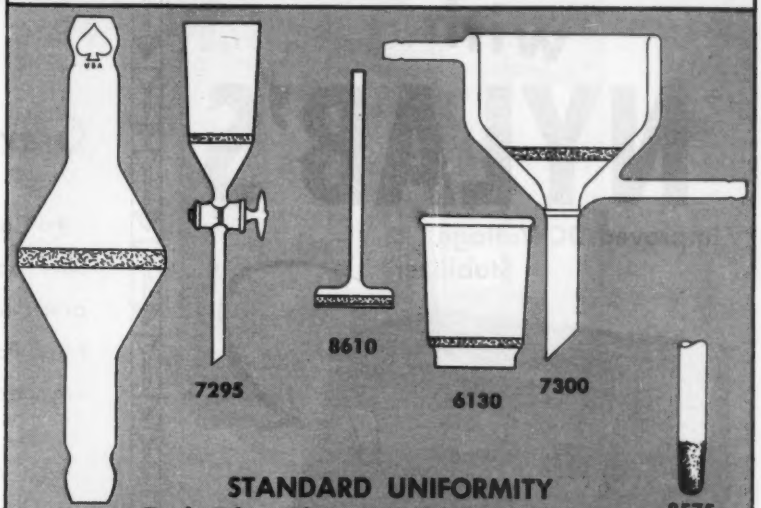

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ing, nuclear physics, and experimental physics. The coming term will be the fifth formal session.

Further information and application forms may be obtained from the Oak Ridge School of Reactor Technology, P. O. Box P, Oak Ridge, Tennessee.

Hot Plate for Heavy Duty Service

Thermo Electric Manufacturing Co., 471 Huff St., Dubuque, Iowa, has just announced a new electric hot plate especially designed for hard use over prolonged periods.

According to the manufacturer, the new hot plate, type 2600, will support heavy loads and its smooth, cast iron top plate is serviceable for applications where an aluminum top plate is not suitable.

The body of stainless steel is formed in two sections separated by an insulating plate which minimizes heat transfer into the bottom section. The heating plate, with an inch thickness of block insulation, is suspended in the top section with ventilating air channels underneath and on all four sides. This construction insulates the control switch and supporting table against heat from the top plate.

Temperature is regulated by a four-heat switch, providing temperatures of 400°, 535°, 710°, and 930°F.

Prices and detailed information are available from the manufacturer.

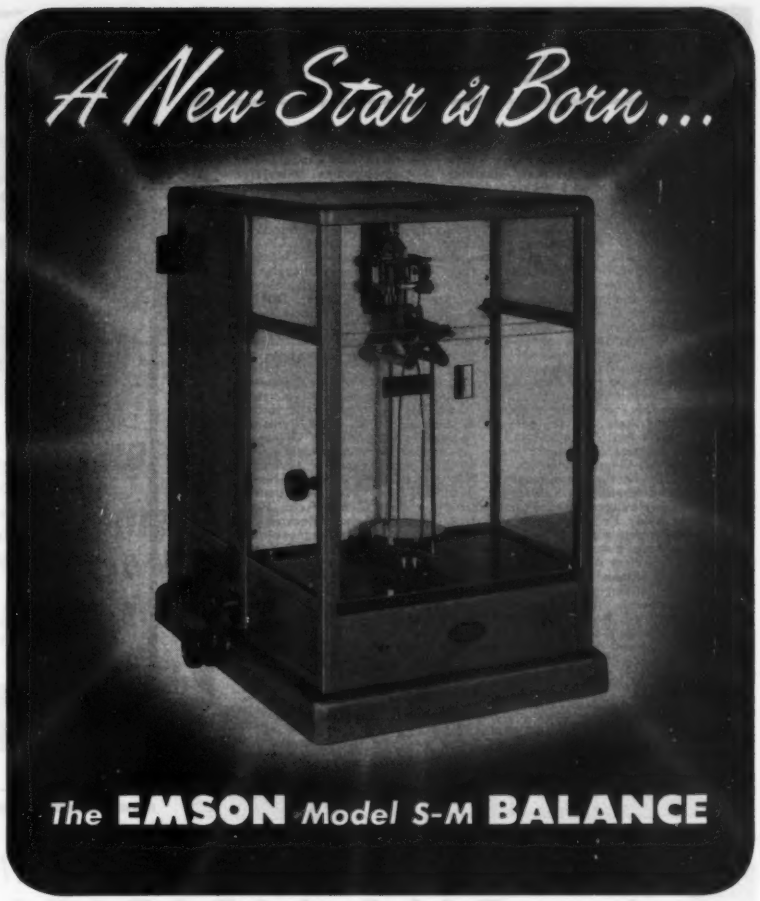
New Literature

● A two-color illustrated brochure showing the features and advantages of the single beam Model 12-C Infrared Spectrometer has just been published by The Perkin-Elmer Corporation. The model is used for routine quality control in chemical laboratories, and is offered at new reduced prices.

Three versions of the Model 12-C are described: (1) a non-recording unit (Model 12-S); (2) a recording unit (Model 12-Cl); and (3) a mobile recording unit (Model 12-C). This last version is mounted on a mobile metal console and may be moved anywhere in a plant for on-the-spot measurements.

Copies of the new brochure may be obtained from The Perkin-Elmer Corporation, Norwalk, Connecticut.

● Over 600 items of interest to research workers in the fields of biology, microbiology, bacteriology, biochemistry, and nutrition are listed in the new 1954 issue of the GBI Catalogue. The following types of products are included: Amino acids, peptides, carbohydrates, nucleates, purines, pyrimidines, enzymes, pH indicators, microbiological and bacteriological media, complete animal test diets, test diet ingredients, and miscellaneous research bio-



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● The fourth issue of the "Nucleus" has just been released by the Nuclear Instrument and Chemical Corp., 229 W. Erie St., Chicago 10, Illinois.

Articles in the issue describe new methods for counting radioactive iodine in the measurement of thyroid function, an article on radioisotope facilities in the general hospital, an article on isotope dilution analysis, and a description of Nuclear-Chicago's new radiochromatographic analyzer.

Copies will be gladly sent on request.

● A new catalog which shows their complete line, has just been published by El-Tronics, Inc., Fifth and Noble Sts., Philadelphia 23, Pennsylvania. Besides illustrations and descriptions of their instruments for measurement of radioactivity, some space is devoted to suggestions for planning nuclear laboratories. Copies of the catalog are available on request.

● E. Machlett & Son has just announced the publication of an attractively illustrated folder entitled "Avoid Costly Breakage with Machlett Polyethylene Laboratory Ware." Included in the folder are 11 "everyday" laboratory items of all sizes ranging from polyethylene policemen to 13-gallon polyethylene carboys. Copies of this folder are available from E. Machlett & Son, 220 E. 23rd St., New York 10, New York.

● A new folder describing the use of Filter Paper Supports as a time-saving aid to filtration has just been issued by Carl Schleicher & Schuell Co., Keene, New Hampshire, manufacturers of high quality analytical filter papers. The folder specifies the advantages and physical properties of filter paper supports, and provides folding instructions with six diagrams. Folder is free upon request.

● Bulletin FW-3, just released by The U. S. Stoneware Co., describes and illustrates The "Cyclonaire," the portable fume washer for low-cost fume removal in plants and laboratories.

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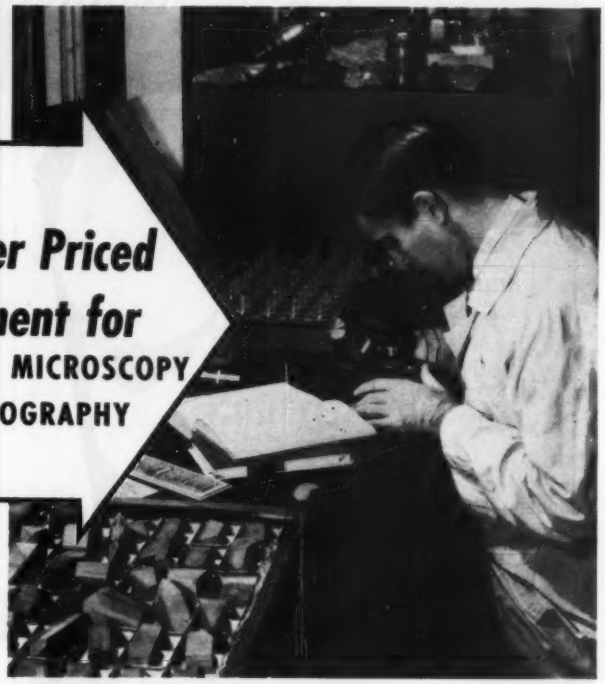

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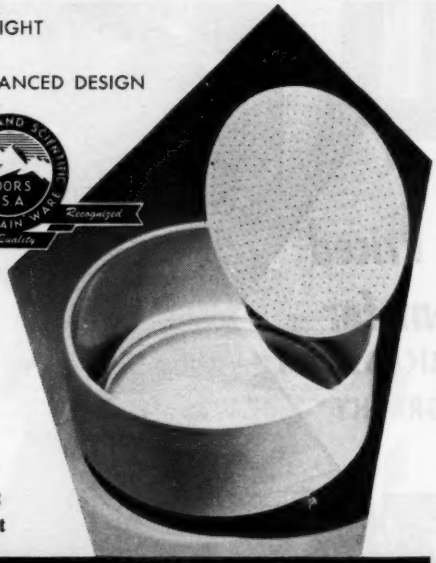

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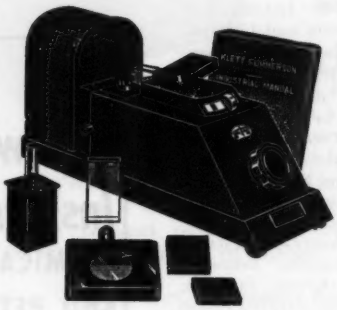

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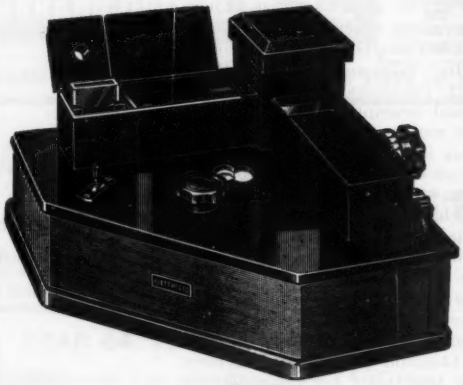

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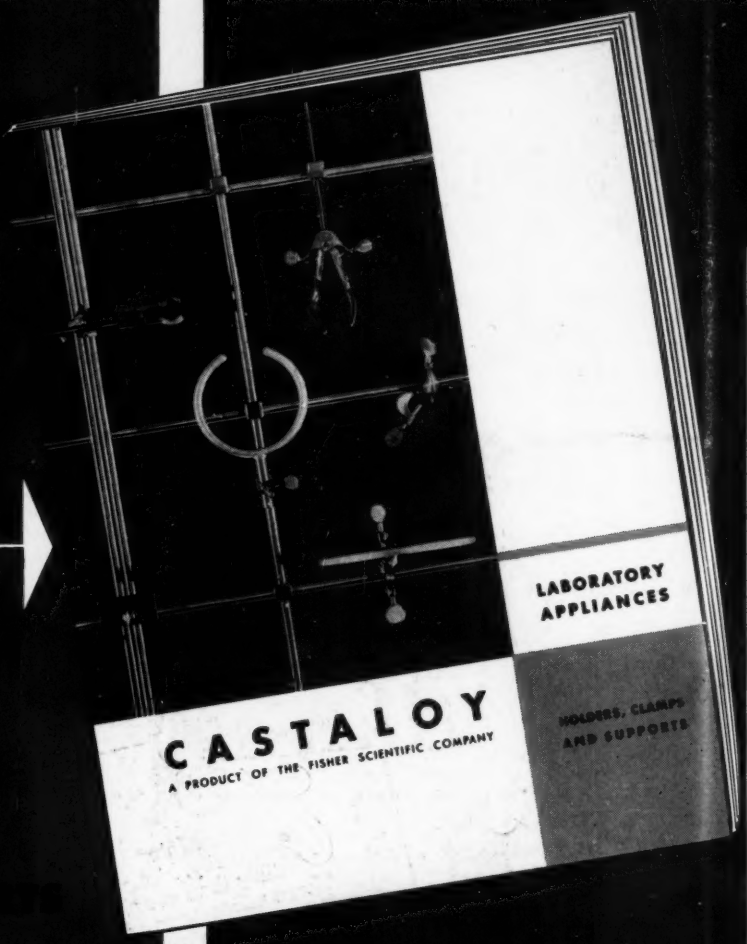

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